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The Abnormality in the Mechanical Behavior of Polyvinyl Acetate-Carbon Tetrachloride Gel

By Kazuyoshi OGINO

(Received February 23, 1959)

It is well known that many polymeric substances are typically visco-elastic: their stress under constant strain decreases continuously with time; i.e. stress relaxation is observed. In this case, it is usual that the stress deteriorates with time, and this is expected from the following consideration: when a specimen is held under a constant strain, the relative position or the configuration of the molecules changes with time so as to attain a more unstrained position, and thus the stress which corresponds to this strain decreases with time. This is the stress relaxation in "normal" condition.

On the other hand, Tobolsky et al. found[1] that some abnormalities in the stress relaxation under constant elongation appear at about 100°C when natural and several synthetic polymers are heated in the air. Further, they thought that the structural or chemical changes are reflected in the visco-elastic behavior of these substances. This phenomenon is known as the chemorheological process.

Many examples of abnormalities in the mechanical properties of polymeric substances have been interpreted as the result of the scission of the network chain or the cross-linking reaction by oxygen in the air*,[2].

The author found that the mechanical behavior of swollen polyvinyl acetate gels, which were cross-linked slightly with diallyl adipate and swollen in several organic solvents, shows abnormality when carbon-tetrachloride was used as a solvent; i.e. their stress *increases* continuously with time when the temperature was raised above 50°C. When one chooses polyvinyl acetate, polymethyl acrylate, polymethyl methacrylate or polystyrene as the polymeric substance, and chloroform, benzene, toluene, carbon tetrachloride or methanol as the solvent, the combination of polyvinyl acetate and carbon tetrachloride is the only system which causes an increase in stress under constant strain. The purpose of this paper is to report this abnormality, and to make a possible interpretation for this phenomenon.

Experimental

Materials.—Commercial monomeric vinyl acetate was shaken several times with aqueous alkaline solution, and with distilled water. This process was repeated three times. The monomer was then distilled under reduced pressure.

Diallyl adipate was synthesized by esterification of allyl alcohol with adipic acid, and was purified by fractional distillation under reduced pressure**.

Carbon tetrachloride was purified by washing with aqueous alkaline solution and by distillation.

Vinyl acetate monomer mixed with cross-linking agent was polymerized thermally in bulk in a sealed glass tube under the presence of benzoyl peroxide as initiator (about 0.5 wt. %). This had been purified by recrystallization. At the beginning of polymerization, the temperature was kept at about 50°C until the contents were solidified, and was then held at 100°C for 12 hr.

The polymer rod was cut into several pieces, about 1 cm. in length, and was brought to the swelling equilibrium in carbon tetrachloride.

Apparatus.—The apparatus used in this

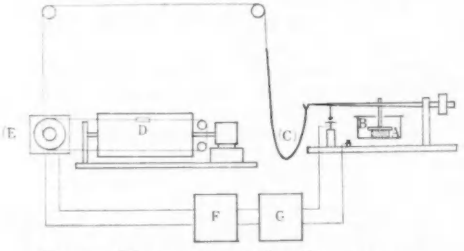

Fig. 1. The apparatus for the measurement of stress relaxation.
A: Specimen. B: Solvent. C: Chain.
D: Rotating drum & pencil.
E: Balancing motor. F: Relay.
G: Amplifying circuit.

1) A. V. Tobolsky and R. D. Andrews, *J. Chem. Phys.*, **13**, 3 (1945).

* The effect of oxygen upon the stress relaxation or creep was studied by the measurement which is known as the intermittent and continuous method.

2) R. D. Andrews, E. E. Hanson and A. V. Tobolsky, *J. Appl. Phys.*, **17**, 352 (1946).

** This cross-linking agent is the same as was used in the previous work; K. Ogino, This Bulletin, **31**, 577 (1958).

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experiment is the same as the one used in the previous work[3], and is shown in Fig. 1.

The temperature of the sample was controlled by circulation of water from a water bath, and was read directly by a thermometer immersed in the solvent. The temperature was so high (about 50°C) that in some cases the fluctuation was observed to some extent, but this did not exceed 1°C.

Results and Discussion

Fig. 2 shows the relation between stress and time at about 50°C under 20% strain. It is clear from this figure that the stress in these gels decreases slightly in the first step and then increases. The degree of this increase in stress becomes larger as the degree of swelling diminishes.

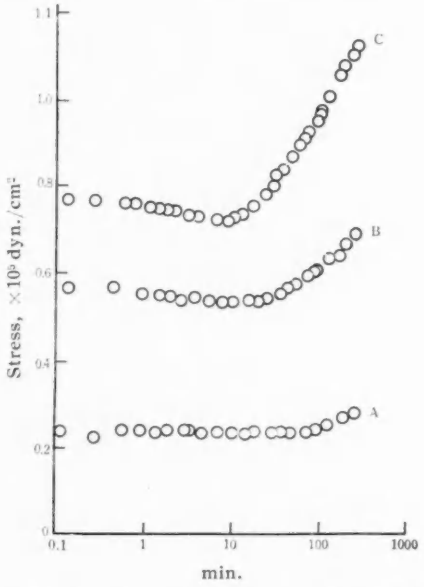

Fig. 2. The relation between stress and time under 20% strain (vertical compression) in CCl_4.
A: Volume fraction 0.24 at 48°C.
B: Volume fraction 0.33 at 49°C.
C: Volume fraction 0.42 at 49°C.

Oxygen from the air can not be considered to be the cause of this abnormality, because this occurs only in the system of polyvinyl acetate and carbon tetrachloride, and does not occur in any other polymer-solvent combinations. It is difficulty to find any reason for the effect of atmospheric oxygen being found in this system alone. The structural difference between vinyl acetate and methyl acrylate is only in the position of the carbonyl group. There must consequently be some special meaning for the vinyl acetate system. This can be interpreted as follows.

It is well known that in the solution polymerization, especially when carbon tetrachloride, carbon tetrabromide, chloroform, sulfur dichloride or mercaptane is chosen as solvent, the chain transfer with solvent molecules occurs very easily and each polymer molecule contains fragments of the solvent[4]. Such a compound is known as telomer, and the reaction is called telomerization. Fig. 3 shows the mechanism of the chain transfer with carbon tetrachloride as an example.

On the other hand, the chain transfer with monomeric vinyl acetate takes place in the scheme as shown in Fig. 4.

$$Mn\cdot + CCl_4 \rightarrow MnCl + \cdot CCl_3$$

$$\cdot CCl_3 + M \rightarrow M\cdot CCl_3\cdot \rightarrow MnCCl_3\cdot$$

$$MnCCl_3\cdot + CCl_4 \rightarrow \underset{\text{(Telomer)}}{Cl\cdot Mn\cdot CCl_3} + \cdot CCl_3$$

Fig. 3. The chain transfer with carbon tetrachloride.

$$R\cdot + CH_2{=}CH(O{-}C{=}O{-}CH_3) \rightarrow \begin{cases} R{-}CH_2{-}CH(O{-}C{=}O{-}CH_3)\cdot & \text{(A)} \\ R{-}H + CH_2{=}CH(O{-}C{=}O{-}\dot{C}H_2) & \text{(B)} \end{cases}$$

Fig. 4. The chain transfer with vinyl acetate.

In this case, it is noticeable that the radical of type B is produced. This is considered to be the cause of the existence of vinyl groups which are connected to the end of the branching along the long chain molecule of polyvinyl acetate[5]. In the case of the other monomers, such as methyl acrylate, methyl methacrylate or styrene, radicals of this type rarely exist. The existence of this radical, and consequently the possibility of the existence of vinyl groups at the end of each branching in polymer is the characteristic feature of vinyl acetate.

Hence, the polymer which has a structure like that shown schematically in Fig.

3) K. Ogino, This Bulletin, **31**, 580 (1958).

4) P. J. Flory, *J. Am. Chem. Soc.*, **59**, 241 (1937); J. W. Breitenbach and H. Maschin, *Z. physik. Chem.*, **A187**, 175 (1940).

5) O. L. Wheeler, E. Iarin and R. N. Crozier, *J. Polymer Sci.*, **9**, 159 (1952).

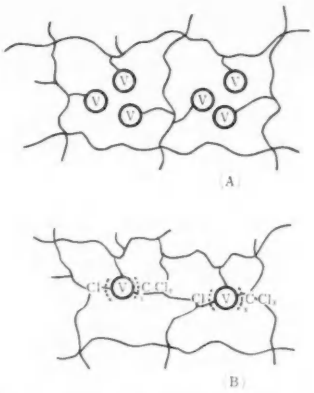

Fig. 5. The schematic diagram to show the internal structure of polyvinyl acetate. (V=Vinyl group)

5A will be produced when vinyl acetate is polymerized thermally in bulk in a sealed tube under the presence of benzoyl peroxide as an initiator. Therefore, when this polymer is brought to the swelling equilibrium with carbon tetrachloride, and is maintained at about 50°C, telomer will be formed between carbon tetrachloride and vinyl groups present at the end of each branching. This feature is shown in Fig. 5B. If this reaction occurs, the effective molecular weight between junction points decreases, and so the stress will increase. In order that this reaction, telomerization, may take place, it is necessary that radicals exist in this system. This postulation seems to be satisfied because the initiator which was added initially into the monomer will still remain undecomposed in the polymer, and further, it is demonstrated, for example, by Ingram[6], that radicals which are created in the course of polymerization will remain unchanged.

To confirm this postulation, the mechanical property of polyvinyl acetate, which was swollen at room temperature in carbon tetrachloride with 5% bromine added, was investigated. By this treatment, vinyl groups may be saturated and radicals may be consumed by bromine; i.e. it may be considered that the cause which provokes telomerization will be removed. This result is shown in Fig. 6. It is clear that after the treatment with bromine solution the "normal" relaxation

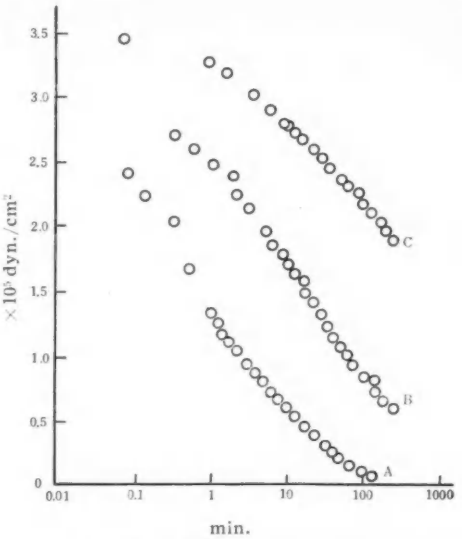

Fig. 6. The relation between stress and time under 20% strain after the treatment by bromine solution in carbon tetrachloride.

of stress is observed. The volume fraction of polymer in bromine solution is larger than that in carbon tetrachloride. This may be due to the polar effect of substituted bromine atoms.

If it may be assumed that the abnormality observed in the system polyvinyl acetate-carbon tetrachloride gel arises from telomerization between vinyl groups and solvent, it is expected that when chloroform is used as a solvent a similar abnormality will be observed. But, as shown in Fig. 7, this was not observed. This may be due to the fact that chloroform is a good solvent for polyvinyl acetate and the degree of swelling becomes very great, so the chain molecules will be fairly far apart from each other in this solvent compared with the case in carbon tetrachloride***.

Tobolsky et al. showed that the splitting or reforming reaction of cross-linkages by oxygen occurs between chain molecules[7], and that if the number of splits per cubic centimeter is a linear function of time, the decay of stress follows the Maxwellian

6) D. J. E. Ingram et al., *Trans. Faraday Soc.*, **51**, 409 (1958).

*** Tobolsky et al. found that the effect of oxygen upon the mechanical property was not observed in swollen polymer, and thought that this might be due to the greater distance of chain molecules in the swollen state than in the dry state[7].

7) A. V. Tobolsky, D. Metz and R. B. Mesrobian, *J. Am. Chem. Soc.*, **72**, 1942 (1950).

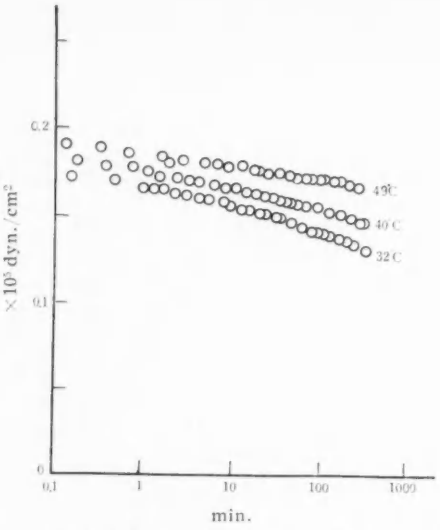

Fig. 7. The relation between stress and time in chloroform. (The volume fraction: 0.020)

decay law[8], or

$$f(t) = f(0) \exp(-kt)$$

where $f(0)$ is the stress at time zero, $f(t)$ the stress at time t, and k the rate constant.

Now, for the system polyvinyl acetate-carbon tetrachloride gel, if a is the number of vinyl groups at time zero between junction points, and x of this group are consumed at time t by telomerization, the following equation can be postulated because the rate of telomerization, dx/dt, will be primarily dependant upon the distance between chain molecules[1], and as the reaction proceeds, the chance of two vinyl groups meeting with each other will increase by the presence of newly formed cross-linkage. Thus, the rate of reaction will be proportional to the number of vinyl groups which have been cross-linked; i. e.

$$dx/dt = kx$$

therefore,

$$\ln(x/a) = kt$$

The stress at time t can be considered to be proportional to the number of cross-linkages, x, which are formed between junction points, and so,

$$\ln\{f(t)/f(0)\} = kt$$

Thus, if one plots the results of Fig. 2 as $\ln(f/f_0)$ against t, the curves of Fig. 8 are obtained. The slope in each curve is identical with the rate constant, k, if the term of stress relaxation is neglected.

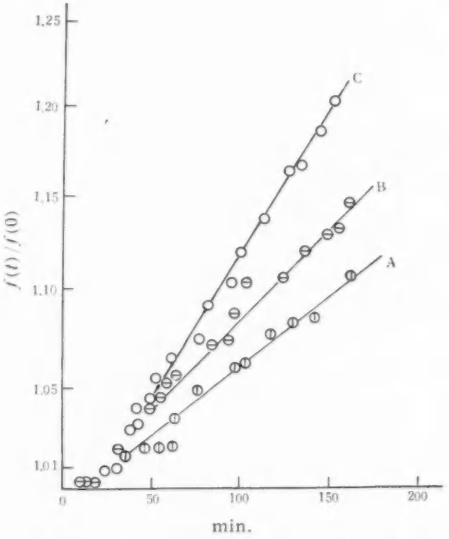

Fig. 8. The plot of $\ln\{f(t)/f(0)\}$ against t at about 50°C.

The abnormality in the mechanical behavior of polyvinyl acetate-carbon tetrachloride gel was interpreted here by telomerization between vinyl groups and solvent.

The author wishes to express his indebtedness to Professor H. Akamatu and Assistant Professor T. Nakagawa for their interest and support, and to Dr. N. Inamoto for his helpful advice and criticism concerning this experiment.

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8) M. D. Stern and A. V. Tobolsky, *J. Chem. Phys.*, **14**, 93 (1946).

Effect of Ionization on the Behavior of Insoluble Monolayers

By Shoichi IKEDA and Toshizo ISEMURA

(Received March 23, 1959)

It has been observed experimentally that an insoluble monolayer of electrolyte is more condensed on an aqueous subphase of higher concentration of salt while it is more expanded on that of lower concentration. Such an effect of salt on the behavior of ionized monolayer was first elucidated by Davies[1] in the light of the theory of electric double layer, which was based on the Gouy-Chapman's theory of diffuse double layer developed by Derjaguin and Landau[2] and Verwey and Overbeek[3]. Investigations on ionized monolayers have been carried out further along this line[4,5].

In the present paper the authors will show that the same results can be derived from a simpler thermodynamic consideration as well as from the electrostatic theory. The present theory is not only more intuitive and tractable but also is a more general approximation, although it assumes an uncertified model.

An insoluble monolayer may be supposed to be a two-dimensional solution in a surface phase, in which the monolayer substance behaves as a solute, apart from its non-polar side chains. It exerts a surface pressure for maintaining thermodynamic equilibrium with the bulk phase. Thus, for an electrolyte monolayer it may be assumed that its ionized groups are dissolved uniformly in a "surface phase" with a definite thickness, δ, and ions of salt in the aqueous subphase are distributed between the surface and bulk phases, counter ions being concentrated in the surface phase and co-ions being repelled from there into the bulk phase. The distribution of ions between the two phases will be first evaluated by an analogy to the membrane equilibrium and then by an improved approximation. The difference in ionic concentrations between the two phases resulting from the ionization of monolayer contributes to both surface pressure and potential. These contributions will be calculated by means of a thermodynamic procedure.

Consider a uni-univalent type of salt and a monolayer substance whose molecule dissociates into an insoluble cation carrying i-univalent ionized groups and i univalent anions common with those of the salt. The ionized groups of the monolayer are assumed to be uniformly distributed in the surface phase. Since the surface phase can not be defined from the present theory alone, its thickness, δ, must be assigned so as to cover the effective thickness of the diffuse double layer, as seen later.

Membrane Equilibrium for Ionized Monolayer

In the present model it is assumed that the boundary between the surface and bulk phases behaves like a semipermeable membrane in osmotic equilibrium and, to the first approximation, the distribution of diffusible ions between these phases is governed by conditions similar to those in Donnan's membrane equilibrium in colloidal solution[6]. That is, electrochemical potentials of each diffusible ion in both phases are put equal. In the expression of the electrochemical potential functions, activities may be substituted by concentrations, unless they are very high.

Let the concentrations of cation and anion of salt be $\bar{n}_+$ and $\bar{n}_-$ (ions per cm^3) in the surface phase, respectively, and those of both ions equally n in the bulk phase. If the electrostatic potential of diffusible ions in the surface phase relative to that in the bulk phase is ψ_D, conditions for equilibrium are given by

$$\begin{aligned} kT\ln\bar{n}_+ + e\psi_D &= kT\ln n \\ kT\ln\bar{n}_- - e\psi_D &= kT\ln n \end{aligned} \qquad (1)$$

where e is the elementary charge, k the

1) J. T. Davies, *Proc. Roy. Soc.*, **A208**, 224 (1951).
2) B. Derjaguin and L. Landau, *Acta Physicochim.*, **14**, 633 (1941).
3) E. J. W. Verwey and J. Th. G. Overbeek, "Theory of the Stability of Lyophobic Colloids", Elsevier, Publishing Co., Inc., New York (1948).
4) K. Hamaguchi and T. Isemura, This Bulletin, **28**, 9 (1955).
5) J. N. Phillips and E. Rideal, *Proc. Roy. Soc.*, **A232**, 159 (1955).
6) F. G. Donnan and E. A. Guggenheim, *Z. physik. Chem.*, **A162**, 346 (1932).

Boltzmann constant and T the absolute temperature. Furthermore, it is assumed that the surface phase remains electrically neutral, i.e.

$$\bar{n}_+ + \frac{i\Gamma_M}{\delta} = \bar{n}_- \tag{2}$$

where Γ_M (ions per cm^2) is the surface concentration of non-diffusible cations, each with i univalent ionized groups, in the surface phase. From Eqs. 1 and 2 the equilibrium concentrations of diffusible ions are obtained as

$$\begin{aligned}\bar{n}_+ &= \frac{1}{2}\left\{-\frac{i\Gamma_M}{\delta} + \sqrt{\left(\frac{i\Gamma_M}{\delta}\right)^2 + 4n^2}\right\} \\ \bar{n}_- &= \frac{1}{2}\left\{\frac{i\Gamma_M}{\delta} + \sqrt{\left(\frac{i\Gamma_M}{\delta}\right)^2 + 4n^2}\right\}\end{aligned} \tag{3}$$

They can also be written as

$$\begin{aligned}\bar{n}_+ &= n\exp(-e\phi_D/kT) \\ \bar{n}_- &= n\exp(e\phi_D/kT)\end{aligned} \tag{4}$$

where

$$i\Gamma_M = 2n\delta\sinh\frac{e\phi_D}{kT} \tag{5}$$

The surface excesses of diffusible ions may be defined as

$$\begin{aligned}\Gamma_+ &= \delta(\bar{n}_+ - n) \\ \Gamma_- &= \delta(\bar{n}_- - n)\end{aligned} \tag{6}$$

and the surface concentration of the ionized group is

$$i\Gamma_M = 1/A \tag{7}$$

where A is the area per ionized group.

In order to determine the thickness of the surface phase, δ, and the potential of ionized groups of monolayer, ϕ_M, one must take account of the results of the theory of diffuse double layer. According to the theory, concentrations of diffusible ions at the depth, x, below the surface, where the electrostatic potential is ϕ, are given by

$$\begin{aligned}n_+ &= n\exp(-e\phi/kT) \\ n_- &= n\exp(e\phi/kT)\end{aligned} \tag{8}$$

where n is the concentration of each ion or salt far away from the surface. Their surface excesses may be defined by

$$\begin{aligned}\Gamma_+ &= \int_0^\infty (n_+ - n)\mathrm{d}x \\ \Gamma_- &= \int_0^\infty (n_- - n)\mathrm{d}x\end{aligned} \tag{9}$$

which lead to

$$\begin{aligned}\Gamma_+ &= \frac{2n}{\kappa}\left\{\exp\left(-\frac{e\phi_G}{2kT}\right) - 1\right\} \\ \Gamma_- &= \frac{2n}{\kappa}\left\{\exp\left(\frac{e\phi_G}{2kT}\right) - 1\right\}\end{aligned} \tag{10}$$

Here ϕ_G is the potential at the surface, $x=0$, and κ is the Debye-Hückel parameter

$$\kappa^2 = \frac{8\pi ne^2}{\varepsilon kT} \tag{11}$$

ε being the dielectric constant. As for the distribution of diffusible ions, the present treatment corresponds to an averaged procedure of the theory of diffuse double layer. Thus, equating Eq. 6 to Eq. 10, it follows that

$$\delta = 2/\kappa \tag{12}$$

and

$$\phi_D = \phi_G/2 \tag{13}$$

The electrostatic potential of ionized groups of monolayer, ϕ_M, should be equal to the Gouy potential, ϕ_G. Hence, it is twice as high as the electrostatic potential of diffusible ions, or the membrane potential, ϕ_D.

$$\phi_M = 2\phi_D \tag{14}$$

It may be assumed generally in the treatment of ionized monolayers based on the present model of surface phase that the thickness of surface phase is given by $2/\kappa$ and the electrostatic potential of ionized groups is twice as high as that of diffusible ions.

Improved Approximation for the Distribution of Ions

The distribution of diffusible ions obtained in the previous section has been derived from a simple assumption that the surface phase is electrically neutral. In this section one will develop an approximate method when this assumption is removed.

When the surface and bulk phases are distinguished from each other, the electrostatic potential, ϕ, of diffusible ions follows the Poisson equations

$$\frac{\mathrm{d}^2\phi}{\mathrm{d}x^2} = -\frac{4\pi e}{\varepsilon}\left(\frac{i\Gamma_M}{\delta} + n_+ - n_-\right)$$

for $x \leq \delta$ (surface phase) (15)

$$= -\frac{4\pi e}{\varepsilon}(n_+ - n_-)$$

for $x \geq \delta$ (bulk phase) (16)

where $\delta = 2/\kappa$, and their concentrations are given by equations formally identical with

Eq. 8. Eqs. 8 and 15 imply that the surface phase is not always electrically neutral.

In order to solve the Poisson-Boltzmann equations, Eqs. 15 and 16 with Eqs. 8, it will be assumed that the surface phase deviates slightly from being electroneutral. In such a case the "λ-method", which was devised for solving the problem of polyelectrolyte solution[7], might be applied to the present equations. Then a quantity λ is defined as

$$\frac{i\Gamma_M}{\delta} + n_+ - n_- = \frac{i\Gamma_M}{\delta}\lambda \tag{17}$$

$$\lambda \ll 1 \tag{18}$$

Evidently, the problem is reduced to that of the membrane equilibrium, if $\lambda=0$. From Eqs. 8 and 17, it follows that

$$\sinh\frac{e\psi}{kT} = \frac{i\Gamma_M}{2n\delta}(1-\lambda) \tag{19}$$

Expanding $e\psi/kT$ in a series of λ using Eq. 19 and ignoring the terms higher than λ, one obtains

$$\frac{e\psi}{kT} = \ln\frac{i\Gamma_M+\sqrt{(i\Gamma_M)^2+4(n\delta)^2}}{2n\delta} - \frac{i\Gamma_M\lambda}{\sqrt{(i\Gamma_M)^2+4(n\delta)^2}} \tag{20}$$

and

$$\lambda = \frac{\sqrt{(i\Gamma_M)^2+4(n\delta)^2}}{i\Gamma_M}\left[-\frac{e\psi}{kT} + \ln\frac{i\Gamma_M+\sqrt{(i\Gamma_M)^2+4(n\delta)^2}}{2n\delta}\right] \tag{21}$$

Then, instead of Eq. 15, one has a linear equation

$$\frac{d^2\lambda}{dx^2} = \chi^2\lambda \tag{22}$$

or

$$\frac{d^2\psi}{dx^2} = \chi^2(\psi-\psi_D) \tag{23}$$

where

$$\chi^2 = \frac{4\pi e^2}{\varepsilon kT}\sqrt{\left(\frac{i\Gamma_M}{\delta}\right)^2+4n^2} \tag{24}$$

and

$$\frac{e\psi_D}{kT} = \ln\frac{i\Gamma_M+\sqrt{(i\Gamma_M)^2+4(n\delta)^2}}{2n\delta} \tag{5a}$$

The most general boundary conditions for Eqs. 15 and 16 are given by

$$(d\psi/dx)_{x=0} = 0 \tag{25}$$

ψ and $d\psi/dx$: continuous at $x=\delta$ (26)

and

$$\psi_{x=\infty} = (d\psi/dx)_{x=\infty} = 0 \tag{27}$$

Under these conditions one can obtain solutions which correspond to those derivd by Lifson[8] and Nagasawa and Kagawa[9] for the polyelectrolyte solution. For the sake of simplicity, however, a simpler condition

$$\psi_{x=0} = 0 \tag{26a}$$

is chosen here instead of the second condition (26). This means that $\psi=0$ and $n_+ = n_- = n$ in the bulk phase ($x \geq \delta$). Thus the surface phase ($x \leq \delta$) may be treated separately. The solutions of Eqs. 22 and 23 are found to be

$$\lambda = \frac{\sqrt{(i\Gamma_M)^2+4(n\delta)^2}}{i\Gamma_M}\frac{e\psi_D}{kT}\frac{\cosh\chi x}{\cosh\chi\delta} \tag{28}$$

and

$$\psi = \psi_D\left(1-\frac{\cosh\chi x}{\cosh\chi\delta}\right) \tag{29}$$

respectively.

After this, one will be concerned with the mean concentrations and the mean potential of ions in the surface phase. By a simple averaging procedure or by Gauss's theorem of electrostatics, the mean value of λ is calculated to be

$$\langle\lambda\rangle = \frac{\sqrt{(i\Gamma_M)^2+4(n\delta)^2}}{i\Gamma_M}\frac{e\psi_D}{kT}\frac{\tanh\chi\delta}{\chi\delta} \tag{30}$$

The mean concentrations of cation and anion in the surface phase are then represented by

$$\begin{aligned}\langle n_+\rangle &= \frac{1}{2}\left\{-\frac{i\Gamma_M}{\delta}+\sqrt{\left(\frac{i\Gamma_M}{\delta}\right)^2+4n^2}\right\}\left\{1+\frac{i\Gamma_M\langle\lambda\rangle}{\sqrt{(i\Gamma_M)^2+4(n\delta)^2}}\right\}\\ \langle n_-\rangle &= \frac{1}{2}\left\{\frac{i\Gamma_M}{\delta}+\sqrt{\left(\frac{i\Gamma_M}{\delta}\right)^2+4n^2}\right\}\left\{1-\frac{i\Gamma_M\langle\lambda\rangle}{\sqrt{(i\Gamma_M)^2+4(n\delta)^2}}\right\}\end{aligned} \tag{31}$$

respectively, and their surface excesses are defined by

$$\begin{aligned}\Gamma_+ &= \delta(\langle n_+\rangle - n)\\ \Gamma_- &= \delta(\langle n_-\rangle - n)\end{aligned} \tag{32}$$

respectively. The mean electric potential of diffusible ions in the surface phase is given by

$$\langle\psi\rangle = \psi_D\left(1-\frac{\tanh\chi\delta}{\chi\delta}\right) \tag{33}$$

7) F. Oosawa, N. Imai and I. Kagawa, *J. Polymer Sci.*, **13**, 93 (1953).

8) S. Lifson, *J. Chem. Phys.*, **27**, 700 (1957).

9) M. Nagasawa and I. Kagawa, This Bulletin, **31**, 961 (1958).

The potential of ionized groups of monolayer is assumed to be defined by

$$\psi_M = 2\langle\psi\rangle \tag{34}$$

as described before. Then one has

$$\langle n_+\rangle/n = n/\langle n_-\rangle = \exp(-e\psi_M/2kT) \tag{35}$$

Contribution of Ionization to Surface Pressure and Potential

When a monolayer is ionized and charged positively, diffusible ions in aqueous subphase become distributed between the surface and the bulk phase, as given by Eq. 3 or 31, and the electrostatic potential of the monolayer becomes higher than that of the diffusible ions in the bulk phase by the amount ψ_M, as given by Eq. 14 or 34. The thermodynamic equilibrium is established by accompanying the decrease in surface free energy, i.e. the increase of surface pressure. The relationship between the increment of surface pressure and the ionic concentrations will be described by an equation such as the Gibbs absorption isotherm. At a constant surface concentration of monolayer, the surface pressure, Π_i, due to the ionization of monolayer can be expressed by

$$d\Pi_i = kT(\Gamma'_+ + \Gamma'_-)d\ln n + i\Gamma'_M d(e\psi_M) \tag{36}$$

In the following formula one will carry out the integration of Eq. 36 in the case of the λ-approximation, since the results from the treatment of membrane equilibrium can be derived as a limiting case. Inserting Eqs. 31 and 32 into Eq. 36 and neglecting the terms higher than λ, it may be written as

$$d\Pi_i = kT\left\{-2n\delta + \sqrt{(i\Gamma'_M)^2 + 4(n\delta)^2} - \frac{(i\Gamma'_M)^2\langle\lambda\rangle}{\sqrt{(i\Gamma'_M)^2 + 4(n\delta)^2}}\right\}d\ln n + i\Gamma'_M d(e\psi_M) \tag{37}$$

Integration leads to

$$\Pi_i = 2kT\left\{-2n\delta + \sqrt{(i\Gamma'_M)^2 + 4(n\delta)^2} - \frac{(i\Gamma'_M)^2\langle\lambda\rangle}{\sqrt{(i\Gamma'_M)^2 + 4(n\delta)^2}}\right\} - kT(i\Gamma'_M)^2\int_\infty^n \frac{\langle\lambda\rangle}{\sqrt{(i\Gamma'_M)^2 + 4(n\delta)^2}}\frac{dn}{n} \tag{38}$$

provided that the integration constant is chosen so as to be $\Pi_i = 0$ at the infinite salt concentration. If the last term with a complicated integral is ignored, it follows that

$$\Pi_i = 2kT(\Gamma'_+ + \Gamma'_-) \tag{39}$$

$$= 2kT\delta(\langle n_+\rangle + \langle n_-\rangle - 2n) \tag{40}$$

In the approximation of membrane equilibrium, $\langle\lambda\rangle = 0$, Eq. 40 reduces to

$$\Pi_i = 2kT\delta(\bar{n}_+ + \bar{n}_- - 2n) \tag{41}$$

Eqs. 40 and 41 represent a colligative nature of surface pressure at a low surface concentration of monolayer. Eqs. 40 and 41 can be rewritten by the use of measurable quantities as

$$\Pi_i = 2kT\left\{-\frac{4n}{\kappa} + \sqrt{\frac{1}{A^2} + \left(\frac{4n}{\kappa}\right)^2} - \frac{1}{A^2}\frac{\langle\lambda\rangle}{\sqrt{\frac{1}{A^2} + \left(\frac{4n}{\kappa}\right)^2}}\right\} \tag{42}$$

and

$$\Pi_i = 2kT\left\{-\frac{4n}{\kappa} + \sqrt{\frac{1}{A^2} + \left(\frac{4n}{\kappa}\right)^2}\right\} \tag{43}$$

respectively, and by the use of the electrostatic potential of monolayer the above two equation become as follows:

$$\Pi_i = 4n\delta kT\left(\cosh\frac{e\psi_M}{2kT} - 1\right) \tag{44}$$

Eq. 44 in the case of $\langle\lambda\rangle = 0$ is in complete agreement with the equation derived from the theory of diffuse double layer

$$\Pi_i = \frac{8nkT}{\kappa}\left(\cosh\frac{e\psi_G}{2kT} - 1\right) \tag{45}$$

which should be expected if Eqs. 12–14 hold.

The situation that the same results follow both from the treatments of membrane equilibrium and of diffuse double layer has also been noticed in the theory of polyelectrolyte solution[9,10]. Further, it would be more plausible to assume that $\delta = 2/\kappa$, although it had always been assumed that $\delta = 1/\kappa$[11].

If the surface pressure of unionized monolayer is Π_0, the observed surface pressure of ionized monolayer can be expressed by

$$\Pi = \Pi_0 + \Pi_i \tag{46}$$

Thus, the surface pressure of ionized

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TABLE I

$T=293°$K, $\varepsilon=80$

1) Octadecyltrimethylammonium chloride on NaCl

$A=85$ A^2 per long chain ion

n mol./l.	δ A	Π_i(Eq. 43)	Π dyn./cm.	Π_0	ψ_D mV.	$\bar{n}_+$ mol./l.	$\bar{n}_-$
0.033	33.6	8.46	5.8	−2.66	72.4	0.00188	0.583
0.10	19.3	7.80	5.3	−2.50	62.0	0.00853	1.17
0.50	8.62	6.18	3.8	−2.38	42.4	0.0935	2.69
2.0	4.32	4.28	2.7	−1.58	27.2	0.676	5.88

$\Pi_0=-3.5$ (Davies)

2) Copoly-1 : 3 : 1-(L-lysine, L-phenylalanine, L-glutamic acid) on KCl *in* 0.005 N HCl

$n=n_{HCl}+n_{KCl}$

$A=20\times5$ A^2 per ionized group (L-lysyl residue)

n mol./l.	δ A	Π_i(Eq. 43)	Π dyn./cm.	Π_0	ψ_D mV.	n_+ mol./l.	n_-
0.040	30.5	6.90	0.65	−6.25	64.5	0.00347	0.581
0.075	22.3	6.56	0.55	−6.11	57.4	0.00817	0.780
0.135	16.6	6·16	0.30	−5.86	50.4	0.0189	1.033
0.405	9.59	5.12	0.05	−5.07	37.8	0·0915	1.843

$\Pi_0=-5.8$ (Hamaguchi and Isemura)

monolayer is higher at lower salt concentration, and, conversely, it is lower at higher salt concentration. At sufficiently high salt concentrations, $\Pi_i=0$ and, accordingly, $\Pi=\Pi_0$. (A polyelectrolyte monolayer exerts an additional surface pressure due to the elastic deformation of polymer chains on ionization, but the inference mentioned here remains unaltered.)

The surface potential of ionized monolayer measured experimentally has the form[1,12]

$$\Delta V=\frac{4\pi\mu}{A}+\psi_M \tag{47}$$

where μ is the surface moment per ionized group. At sufficiently high salt concentrations, $\psi_M=0$ and, accordingly, $\Delta V=4\pi\mu/A$. At low salt concentrations,

$$\left(\frac{\partial\Delta V}{\partial\ln n}\right)_{\Pi'_M\text{ or }A}=\left(\frac{\partial\psi_M}{\partial\ln n}\right)_{\Pi'_M\text{ or }A}=-\frac{Tk}{e} \tag{48}$$

as already found by Crisp[13].

Comparison with Experiments

The results obtained above from either treatment for ionized monolayers, the approximation of membrane equilibrium or the λ-method, can be readily examined with experimental data, by comparing the values of Π_0 and μ at various salt concentrations, which can be evaluated by subtracting the calculated values of Π_i and ψ_M from the observed values of Π and ΔV, respectively. If the treatments were valid, the Π_0 and μ values should be independent of salt concentration. One has applied the procedure to the available data on surface pressure of two typically different monolayers, i.e. those of octadecyltrimethylammonium chloride*,[1] and of copoly-1 : 3 : 1-(L-lysine, L-phenylalanine, L-glutamic acid)**,[4].

For the approximation of membrane equilibrium, using Eq. 43 for Π_i, the results as shown in Table I are obtained. It can be seen that the Π_0 values are not independent of salt concentration. Further, all these values are found to be negative. The negative Π_0 values imply that the corresponding unionized monolayers would contract in themselves rather than spread on aqueous surfaces. Davies' suggestion that the ionized monolayers would be condensed into "islands" or micelles is not valid, since the ionized monolayers do not contract but only form condensed films on strong salt solutions. This inconsistency may be ascribed to an overestimate of Π_i values. The too high contribution of ionization to monolayer properties

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13) D. J. Crisp, Research, "Surface Chemistry", Butterworths Scientific Publications, London (1949), p. 65.

* For this monolayer, a constant value of μ was noticed by Davies[1]. However, the μ value appears to be insensitive to salt concentration.

** If the deformation of polymer chains on ionization is taken into account, the Π_0 values would be lower than those in Table I, in which this contribution is not involved.

comes from the distribution of counter ions being too much concentrated in the surface phase and of co-ions being too much repelled from there. Indeed, the present approximation sometimes leads to concentration of counter ions in the surface phase being more than ten times as high as that in the bulk phase.

It can be expected that this difficulty will be partly avoided by removing the assumption of the electroneutral surface phase. The λ-approximation has led to the surface pressure due to ionization given by Eq. 42, which is lower than that obtained by the approximation of membrane equilibrium, Eq. 43, by the amount

$$\frac{kT}{A}\ln\left[\frac{1/A+\sqrt{(1/A)^2+(4n/\kappa)^2}}{-1/A+\sqrt{(1/A)^2+(4n/\kappa)^2}}\right]\times\frac{\kappa}{2\zeta}\tanh\frac{2\zeta}{\kappa}$$

To confirm this, the data for the monolayer of octadecyltrimethylammonium chloride has been treated by Eq. 42 in a manner as previously. The results are shown in Table II. It can be seen that the Π_0 values are independent of salt concentration and are always positive. Thus, the inconsistency which was encountered previously in the method of membrane equilibrium is not revealed in the λ-approximation.

TABLE II

Octadecyltrimethylammonium chloride on NaCl, $T=293$ K, $\varepsilon=80$

$A=85$ A^2 per long chain ion

n mol./l.	Π_i(Eq. 42) dyn./cm.	Π	Π_0	$\langle\lambda\rangle$
0.033	3.87	5.8	1.93	0.487
0.100	2.99	5.3	2.31	0.509
0.50	1.40	3.8	2.40	0.539
2.0	0.34	2.7	2.36	0.523

The advantage of the λ-method is, however, only superficial. When the surface concentration of monolayer is not low enough, the last term of an integral in Eq. 38, which can not be easily estimated, becomes significant. Moreover, it is found from Table II that all the $\langle\lambda\rangle$ values are about 0.5 and incompatible with the fundamental assumption, Eq. 18. It may, therefore, be stated that the λ-method, as well as the approximation of membrane equilibrium, can not explain completely the effect of ionization on the typically expanded monolayer of octadecyltrimethylammonium chloride. The method is also found to be insufficient to elucidate consistently the ionization behavior of the condensed monolayer of copoly-1:3:1-(L-lysine, L-phenylalanine, L-glutamic acid).

The main purpose of the theory consists in a description of the experimental fact that an ionized monolayer is more condensed on concentrated salt solutions and is more expanded on dilute solutions. The present theory has, however, given explanations of only a part of the observations that higher salt concentrations reduce surface pressure of an ionized monolayer more than lower salt concentrations do. Generally, an ionized monolayer has an area where the reversal of surface pressure occurs, which is independent of salt concentration but dependent on salt species[5]: at the area larger than this, the surface pressure is lower at higher salt concentrations and at the smaller area it is reversed. Hence, the present theory concerns only the region of large area. It seems likely that for a comprehensive interpretation of the behavior of ionized monolayers the assumption of uniformly distributed ionized groups in the surface phase should be modified and penetration of ions into the surface phase, finite dimension of ions, association effect and other individual characteristics of ions should be taken into account.

Summary

The effect of salt on ionized monolayers is treated with a model of "surface phase", in which ionized groups of monolayers are dissolved uniformly. To obtain the distribution of diffusible ions between the surface and bulk phases, the method of membrane equilibrium and the λ-approximation are employed. The former method is a special case of the latter. The contribution of ionization to surface pressure is calculated thermodynamically. The results derived from the former method are found to be in complete agreement with those derived from the theory of diffuse double layer, if the thickness of surface phase is chosen as $2/\kappa$ and the electric potential of ionized groups is twice as high as the membrane potential. On examining two typically different monolayers, the former method reveals some contradiction, although it explains experimental data qualitively. The latter method, which is more general, can overcome the difficulty and gives reasonable values for surface pressure of an expanded monolayer. It is

found, however, that even the λ-approximation is still unsatisfactory to describe the behavior of ionized monolayers in the range of area with which they are ordinarily concerned.

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The Roles of Prolyl Residue in Polypeptide Monolayers. III. Surface Films of Gelatin

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Collagen and gelatin are unusually rich in prolyl and hydroxyprolyl residues as compared with ordinary globular proteins. Because of the specific structures of these imino acid residues, the configurations of polypeptide chains in these proteins are expected to be quite different from those in other proteins. In fact, such characteristics have been observed in solutions of collagen[1-3] and gelatin[4,5] as well as in collagen fiber[6]. In surface films, if they are spread on aqueous surfaces, collagen and gelatin will likewise show a characteristic behavior.

It was established with synthetic polypetides[7,8] that the presence of prolyl residues in a polypeptide chain makes their surface films more expanded, chiefly due to the decrease in number of hydrogen bonds and, accordingly, the condensed nature of films of ordinary synthetic polypeptides may be ascribed to the hydrogen bonding in films. It has been noticed that most globular proteins form condensed films. If the roles of prolyl residue in polypeptide monolayers are reproduced in protein films, collagen and gelatin should form expanded films on aqueous surfaces.

In the present paper it will be examined by the measurements of surface pressure, potential and viscosity, whether these considerations are valid or not for the surface films of gelatin.

Experimental

Materials.—Gelatin was purified from leaf gelatin of Nihon Hikaku Co., Ltd., by desalting it in acetate buffer at pH 4.8 and then washing it with distilled water. The pH of the solution of gelatin thus obtained was 4.9. Concentrations of gelatin solutions were determined by measuring the dry weight of 0.5% stock solution. Spreading solutions were prepared by diluting the stock solution ten times with distilled water.

Methods.—Surface pressure, potential and viscosity were measured by a surface balance of float type, a vibrating electrode and an oscillating rotatory disk, respectively. Surface moment was calculated from surface potential, using the Helmholtz equation.

To adjust pH of aqueous subphases to 2.0, 5.6 and 11.2, 0.01 N hydrochloric acid, distilled water and 0.01 M potassium carbonate were used, respectively. Purified potassium chloride was added to prevent the film from dissolving into aqueous subphases.

Results

Fig. 1 shows surface pressure-area (Π-A) and surface moment-area (μ-A)

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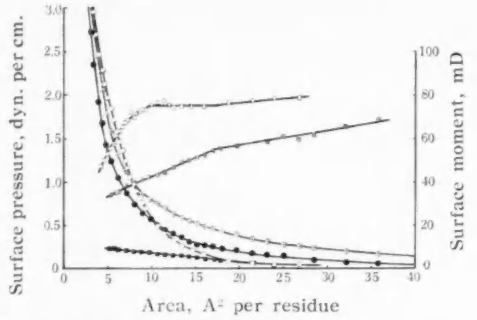

Fig. 1. Surface pressure and moment vs. area curves of gelatin on salt-free solutions at pH 2.0 (⊖, ⊟), 5.6 (○, □) and 11.2 (●, ■): 20°C.

curves of gelatin films on salt-free subphases at three different pH's. Surface pressures of gelatin films on distilled water were scarcely influenced by the temperature of spreading solution and the nature of spreading solvents. Besides a gelatin solution in distilled water at room temperature, a solution in distilled water at 48°C, and solutions in 0.1 M potassium rhodanate, in 40% ethanol and in a mixture of dichloroacetic acid-isopropanol-water (5 : 2 : 3) were examined. Fig. 2 shows the *II-A* and μ-*A* curves of gelatin films on 1 M potassium chloride solutions at three different pH's. On the alkaline side the film had a slight tendency to dissolve into aqueous subphase, when spreading solution was freshly prepared. The surface viscosity-area (η-*A*) curve of the film on 1 M potassium chloride is also shown in Fig. 2.

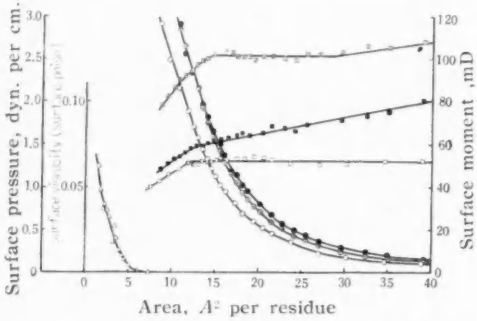

Fig. 2. Surface pressure and moment vs. area curves of gelation on 1 M potassium chloride at pH 2.0 (⊖, ⊟), 5.6 (○, □) and 11.2 (●, ■), and surface viscosity vs. area curve on 1 M potassium chloride at pH 5.6 (△): 20°C.

Discussion

Both collagen and gelatin are composed of about 30% glycyl residues and about 30% prolyl and hydroxyprolyl residues. In solution a collagen molecule exists as a rigid rod-like particle[1,2] which is also found in collagen fiber from X-ray diffraction studies[6]. On the other hand, a gelatin molecule behaves as a random coil like ordinary polymer molecules but unlike a collagen molecule[4,5].

It was reported, however, that, if collagen and gelatin are spread as surface films, they are indistinguishable from each other: collagen spread from its formic acid solution and gelatin from its aqueous and formic acid solutions give identical *II-A* and μ-*A* curves on 30% ammonium sulfate solution[9]. This fact is consistent with the present observations that *II-A* curves of gelatin films are independent of the nature of the spreading solutions.

In spite of its hydrophilic nature, gelatin formed a stable film on distilled water, as already noted[10]. The extent of the spreading of film was very incomplete and not very much influenced by the acididity and alkalinity of aqueous subphases. Such behavior of gelatin film is quite different from those of other protein films[11]. Further, molecular expansion of gelatin as was observed in aqueous solutions[12] was not reflected in its surface films. The surface moment of gelatin was higher on distilled water at pH 5.6 than on aqueous subphases at both sides of this pH. This is not consistent with the idea of titration of surface films[13,11], but is in agreement with the result for collagen film on aqueous solutions, the pH's of which were adjusted by hydrochloric acid[9]. Addition of salt into aqueous subphases caused gelatin films to spread more[14]. Even on 1 M potassium chloride, however, gelatin spread still incompletely and appeared to dissolve on compression. The surface pressures at different pH's were nearly identical on such a concentrated salt solution, as was generally expected from the theory of ionized

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monolayers. Apart from these facts, all the surface films of gelatin were found to be of expanded types.

It has been observed that globular proteins, when spread as monolayers, form condensed films, at least, at the isoelectric point and occupy an area of about 15 A^2 per residue, which would mean that the protein films are in the β-configuration[13,11]. The expanded nature of gelatin films may be attributed to the roles of prolyl residues such as are found in the polypeptide monolayers, i.e. to the reduced number of hydrogen bonds[7]. In surface viscosity behavior was exhibited the general property of expanded films showing that the surface viscosity is only manifest at high surface pressure region[8]. The incomplete spreading and pressure-solubility of gelatin films may come from its hydrophility and specific configuration of polypeptide chains.

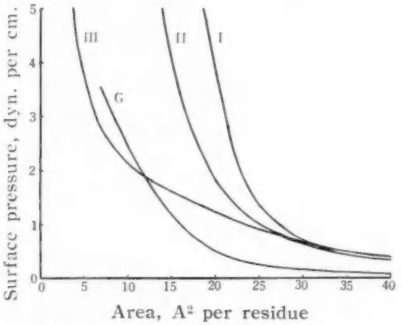

Fig. 3. Comparison of surface pressure-area curve of gelatin with those of some synthetic polypeptides. G: gelatin, I: poly-L-prolyl-L-leucylglycine, II: copoly-1:1:1-(L-proline, L-leucine, DL-alanine), III: poly-L-proline. G and III on 1 M potassium chloride.

Collagen and gelatin molecules were once regarded as consisting of L-prolyl-glycyl-R sequences, on which basis Astbury and Bell[16] suggested a chain configuration in collagen fiber. Recently, Millionova and Andreeva[17] proposed from their X-ray study on poly-glycyl-L-proline that glycyl-L-prolyl sequences are repeated in a collagen molecule. The amino acid analysis on partial hydrolysates of gelatin[18] and collagen[19] has, however, shown that a considerable amount of L-prolyl-L-hydroxyprolyl sequences are found in them, and now it is generally recognized that gelatin and collagen contain these sequences abundantly. At present, a configuration of polypeptide chain in collagen fiber has been established on the basis of the repeated structure of L-prolyl-L-hydroxyprolyl-glycyl sequences[6].

It appears that the surface pressure behavior of gelatin film also supports the presence of these sequences. In Fig. 3 the *II-A* curves of some polypeptide films reported in a previous paper[7] are summarized together with that of gelatin film on 1 M potassium chloride. It will be seen that the extent of expansion or the surface compressibility of gelatin film lies near that of copoly-1:1:1-(L-proline, L-leucine, DL-alanine) and is lower than that of poly-L-proline. In the former copolypeptide L-prolyl-R-L-prolyl sequences are possible and in the latter polypeptide the successive L-prolyl residues exist. Thus, it is considered that a gelatin molecule consists of L-prolyl-R-L-prolyl or L-prolyl-L-prolyl-R sequences. Since some of the prolyl residues in gelatin are substituted by hydroxyprolyl residues and the presence of hydroxyprolyl residues makes a surface film somewhat condensed, the latter sequence, i.e. L-prolyl-L-hydroxyprolyl-glycyl, may be favorable to explain the extent of expansion of gelatin film, in accordance with the results of chemical analysis.

If L-prolyl-L-hydroxyprolyl bonds are assumed to exsist in a gelatin molecule, the effect of salt on gelatin films can be well interpreted following Harrington's suggestion[20], that most of these bonds are *trans* in distilled water and the addition of salt causes the *trans-cis* transformation of these bonds. If the parts of *cis* bond in a gelatin molecule remain on the surface while the parts of *trans* bond dissolve in aqueous phase and the other parts are either on or in aqueous subphase according as their own hydrophility and their surrounding chain configurations, it can be explained why gelatin can form a stale film even on distilled water in spite of its hydrophilic nature. Further, the presence of salt in subphases would stabilize the *cis* bond more than the *trans* bond, causing the *trans-cis* transformation, and make

15) C. W. N. Cumper and A. E. Alexander, *Trans. Faraday Soc.*, **46**, 235 (1950).
16) W. T. Astbury and F. O. Bell, *Nature*, **169**, 662 (1941).
17) M. I. Millionova and N. S. Andreeva, *Biofizika*, **3**, 259 (1958).
18) W. A. Schroeder, L. M. Kay, J. LeGette, L. Honnen and R. C. Green, *J. Am. Chem. Soc.*, **76**, 2783 (1954).
19) T. D. Kroner, W. Tabroff and J. J. McGarr, ibid., **77**, 3356 (1955).
20) W. F. Harrington, *Nature*, **181**, 997 (1958).

films spread more easily. There considerations are consistent with those made for poly-L-proline film previously[7].

Summary

Surface films of gelatin, which is very rich in L-prolyl and L-hydroxyprolyl residues, were examined on salt-free and 1 M potassium chloride solutions at three different pH's by the measurements of surface pressure, potential and viscosity. They were found to spread incompletely but to be of expanded types. The incomplete spreading and the other properties of the films were regarded as a manifestation of the specific configuration of gelatin in films. The expanded nature of the films was attributed to the roles of prolyl residue in gelatin such as observed in polypeptides. The extent of expansion of the films appeared to give evidence to support the results from chemical analysis that a gelatin molecule is composed of a large amount of L-prolyl-L-hydroxyprolyl bonds. The behavior of gelatin films was adequately explained by assuming that the parts of *cis* L-prolyl-L-hydroxyprolyl bond form the film and the parts of *trans* bond dissolve in aqueous subphase.

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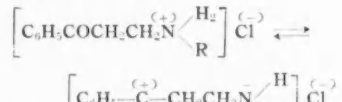
Studies on the Mannich Reaction. III. On the Formation of Piperidine Derivatives (3)

By Norito UCHINO

(Received May 4, 1959)

In the previous papers of this series[1], tautomerism of the Mannich compound involving prototropy was proposed as indicated below.



R = H, CH_3, $C_6H_5COCH_2CH_2$

The present experiment shows a fact which seems to support the above scheme.

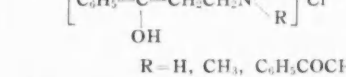
The β-benzoylethylamines[2-4] used are: bis-(β-benzoylethyl)-amine(II), tris-(β-benzoylethyl)-amine(III), 4-oxy-4-phenyl-5-benzoyl-1-(β-benzoylethyl)-piperidine(IV), bis-(β-benzoylethyl)-methylamine(VI) and 4-oxy-4-phenyl-5-benzoyl-1-methyl-piperidine(VII).

$(C_6H_5COCH_2CH_2)_2NH$ (II)

$(C_6H_5COCH_2CH_2)_3N$ (III)

(IV)

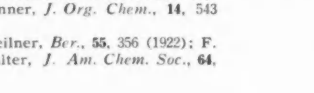
$(C_6H_5COCH_2CH_2)_2NCH_3$ (VI)



(VII)

When bromine water was added to an aqueous solution of hydrochloride of the above Mannich base, yellow precipitates were produced almost quantitatively. The precipitates thus obtained had an irritative odor, probably that of bromine originated from the compounds. The bromine as molecule was also partly removed by washing with water.

In general, bromine may add to a free amine as the following scheme:



1) N. Uchino, This Bulletin, **32**, 1009 (1959).
2) C. Mannich and S. M. Abdullah, *Ber.*, **68**, 113 (1935).
3) J. T. Plati and W. Wenner, *J. Org. Chem.*, **14**, 543 (1949).
4) C. Mannich and G. Heilner, *Ber.*, **55**, 356 (1922); F. F. Blicke and J. H. Burckhalter, *J. Am. Chem. Soc.*, **64**, 451 (1942).

In the present study, such an addition of bromine seems impossible, because the amine is treated as a hydrochloride. Substitution in a benzene nucleus or addition to a double bond which is formed by enolization of a carbonyl group is not probable, considering the ease of evolution of bromine from the addition products and negative ferric chloride test regarding II·HCl or III·HCl.

The bromine compound from the hydrochloride of the Mannich base could be recrystallized from alcohol if the recrystallization was carried out within a little while, bright yellow crystals being obtained which were of an indistinct melting point. When the crystals were heated to a higher temperature, they decomposed and melted to a dark-brown liquid. The recrystallized addition compound still had a smell of bromine, and reduced potassium iodide.

The acid value, the halogen content and the oxidizing power of the recrystallized bromine addition product of II·HCl are summarized in Table I.

TABLE I. ANALYTICAL RESULTS OF BROMINE ADDITION PRODUCT OF II·HCl

	Found ml./g.	Calcd. ml./g.
Acid value (N/10-NaOH)	50.7	21.0[c]
Oxidizing power[a] (N/10-$Na_2S_2O_3$)	24.1	42.0[d]
Halogen content[b] (N/10-$AgNO_3$)	52.6	63.0[d]

a) The bromine addition product was dissolved in alcohol, and potassium iodide was added to the solution. Iodine produced was titrated with sodium thiosulfate solution.

b) Bacon's method was used.

c) Theoretical value of N/10-NaOH consumed for hydrochloric acid which is present as hydrochloride of the addition compound of one mole of bromine with one mole of II·HCl.

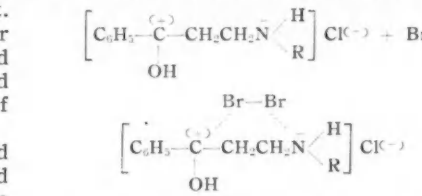
d) Theoretical value for the addition compound of one mole of bromine with one mole of II·HCl.

From the above results, it is considered that at least one mole of bromine is added to one mole of the hydrochloride.

The yellow color of the product from II·HCl or III·HCl disappeared on refluxing the alcoholic solution. On cooling, compound II·HCl was recovered from the solution. When the addition product of II·HCl or III·HCl was treated with alcoholic alkali, base IV was obtained[5]. To obtain the free base of the bromine compound by the alkali treatment, a suspension in water of the additional product of II·HCl or III·HCl was rapidly treated with alkali and the assumed free base produced was immediately extracted with ether. However, the colorless crystals formed proved to be the hydrobromide of II (II·HBr).

The compound II·HCl or III·HCl, however, gave no crystals on the brief treatment with alkali; the ether solution was evaporated to give base IV[5].

On the brief treatment of the bromine addition compound with alkali, a free base containing bromine thus dissolves in ether, and the bromine is partially removed from the original addition product, because the yellow color disappears. Thus the mechanism of the addition of bromine is considered as the following scheme:



The bromine links, in the form of linking astride, on the carbonium ion and on the lone pair of electrons of the nitrogen atom, both of which are formed by the prototropy. When the product is treated with alkali for a little while, the hydrogen chloride and the hydrogen bromide are removed. The free base thus produced may be *N*-bromo-*β*-benzoylethylamine.

The compound of *N*-halogenamine type seems to have an oxidizing power. In the present case, the unstable *N*-bromo-bis-(*β*-benzoylethyl)-amine oxidizes contaminants in the solvent (ether), changing into base II. Base II combines with hydrobromic acid produced, and separates as a hydrobromide.

In order to isolate the unstable *N*-bromoamine, extraction with ether, benzene or carbontetrachloride was attempted without success; the only product obtained was the reduced one II·HBr.

Bromine likewise adds to the free Mannich base. For example, the yellow precipitates readily formed on addition of excessive bromine to an ether solution of base II or III. This product on brief treatment with alkali also yielded the colorless compound II·HBr.

It is known that an amine yields an *N*-bromoamine on treatment with sodium

5) Even if base II or III is produced by the alkali treatment, it changes into base IV; cf. Ref. 2.

hypobromite[6]. Here, compound II·HCl was treated with sodium hypobromite to give II·HBr. This fact also shows the existence of the unstable *N*-bromo-β-benzoylethylamine.

The bromine addition product of III·HCl also gives II·HBr on brief treatment with alkali, probably because of the unstability of the *N*-bromoamine derivative.

Experimental

Addition of Bromine to the Salt of the Mannich Base.—One gram of compound II·HCl or III·HCl was dissolved in 200~300 ml. of water. To the solution was added 500 ml. of bromine water. The yellow precipitates were filtered and dried in vacuo at room temperature in the presence of phosphorous pentoxide; 1.3 g. of bromine addition product of II·HCl or 1.2 g. of that of III·HCl was obtained.

Recrystallization of the Bromine Addition Product.—The bromine addition product, which was obtained from 2.0 g. of II·HCl, was recrystallized from alcohol within a little while to give yellow crystals; yield, 1.5 g. The crystals were analyzed after vacuum-drying at room temperature in the presence of phosphorous pentoxide (Table I).

Decomposition of the Bromine Addition Product by Alcohol.—In boiling alcohol was dissolved 1.5 g. of bromine addition product of II·HCl, and the solution was refluxed for thirty minutes. After being cooled, 1.2 g. of colorless crystals were obtained, which were recrystallized from alcohol acidified with hydrochloric acid to give II·HCl; m. p. and mixed m. p. 173°C.

Anal. Found: C, 67.80; H, 6.52; N, 4.47. Calcd. for $C_{15}H_{20}O_2NCl$: C, 68.02; H, 6.34; N, 4.40%.

The bromine addition product obtained from 1.0 g. of III·HCl was also treated with alcohol giving 0.5 g. of II·HCl; m. p. and mixed m. p. 171~173°C.

Treatment of the Bromine Addition Product with Alcoholic Alkali.—The bromine addition product obtained from 1.0 g. of II·HCl was dissolved in hot alcoholic sodium hydroxide, and the solution was poured into a great volume of water. The aqueous solution which became turbid was allowed to stand for one day. The turbid matter coagulated to a resinous matter. The product was dissolved in hot alcohol, and the free base was converted into hydrochloride by adding hydrochloric acid. After being cooled, the hydrochloride was separated by adding a little ether, filtered, and washed with ether. Yield, 0.1 g. The hydrochloride was recrystallized twice from alcohol giving compound IV·HCl; m. p. and mixed m. p. 196~198°C.

Anal. Found: C, 71.79; H, 6.05; N, 3.18. Calcd. for $C_{27}H_{25}O_3NCl$: C, 72.06; H, 6.27; N, 3.11%.

The bromine addition product obtained from 1.0 g. of III·HCl was also treated with alcoholic alkali to give 0.2 g. of IV·HCl; m. p. and mixed m. p. 197~199°C. The residual alcohol solution was evaporated giving only a dark-brown resinous matter.

Short Treatment of the Bromine Addition Product with Alkali.—The bromine addition product obtained from 2.0 g. of III·HCl was suspended in 100 ml. of water, and an excess of dilute solution of sodium hydroxide was added. The colorless matter produced was quickly extracted with 400 ml. of ether. The organic layer was kept at room temperature; colorless crystals began to separate from the solution. After one day, the crystals were filtered and washed with ether; yield, 0.8 g.; m. p. 166~167°C (from alcohol). The crystals showed a remarkable flame reaction of halogen, and gave precipitates of silver bromide with silver nitrate.

Anal. Found: C, 60.30; H, 5.86; N, 3.88. Calcd. for $C_{15}H_{20}O_2NBr$(II·HBr): C, 59.67; H, 5.56; N, 3.86%.

The crystals were converted into hydrochloride by repeated recrystallization from alcoholic hydrogen chloride to give II·HCl; m. p. and mixed m. p. 172~173°C. From these results, the crystals separated from the ether solution were confirmed to be II·HBr.

The residual ether solution was evaporated only to give a dark-brown resinous matter which could not be distilled at the usual reduced pressure. The resinous matter decomposed at a higher temperature.

The bromine addition product obtained from 2.0 g. of II·HCl gave 1.5 g. of II·HBr in the same way as above; m. p. 166~167°C.

Anal. Found: C, 60.80; H, 5.72; N, 3.89. Calcd. for $C_{15}H_{20}O_2NBr$: C, 59.67; H, 5.56; N, 3.86%.

In the above reaction, ether, benzene or carbontetrachloride was used as an extracting solvent. All these solvents were sufficiently purified just before use. In this case, compound II·HBr was also separated from the solvent, and the yields were 0.8, 0.2 and 0.3 g., respectively.

Reaction of the Salt of the Mannich Base with Alkali.—To 200 ml. of water was added 2.0 g. III·HCl, and an excess of solution of sodium hydroxide. The free base produced was extracted with ether. No crystals separated even when the ether solution was allowed to stand. When the ether solution was evaporated, an oily matter was obtained which solidified after a while. Recrystallization from alcohol gave 1.5 g. of base IV; m. p. and mixed m. p. 149~150°C.

Anal. Found: C, 78.63; H, 6.75; N, 3.65. Calcd. for $C_{27}H_{27}O_3N$: C, 78.42; H, 6.58; N, 3.38%.

Two grams of II·HCl gave 1.1 g. of base IV in the same way as above; m. p. and mixed m. p. 149~150°C.

The Bromine Addition Product of the Free Mannich Base.—To an ether solution of free base III, which was obtained by treating 3.0 g. of III·HCl with a dilute solution of sodium hydroxide for a little while, was added 1.1 g. of bromine.

6) Cf. R. Willstätter and V. Hottenroth, *Ber.*, **37**, 1783 (1904); F. Rashig, *Ann.*, **230**, 223 (1885).

Yellow precipitates produced were filtered, washed, and dried to give 3.5 g. of yellow powder which emitted an irritating odor of bromine. The bromine content of the precipitates was 26.0% [Theoretical ($C_6H_5COCH_2CH_2)_3NBr_2$, 27.9%]. One gram of this addition product was suspended in ether, and an excess of dilute solution of sodium hydroxide was added with shaking. The bromine addition product turned colorless, and dissolved in ether. The ethereal portion was allowed to stand to give 0.2 g. of II·HBr; m. p. 168~169°C (from alcohol).

Anal. Found: C, 59.43; H, 5.63; N, 3.59. Calcd. for $C_{18}H_{20}O_2NBr$: C, 59.67; H, 5.56; N, 3.86%.

The residual ether solution was evaporated to give 0.7 g. of base IV; m. p. and mixed m. p. 149~150°C (from alcohol).

A bromine addition product of base II was produced by the same process as the above one. The bromine content was 44.1% [Theoretical ($C_6H_5COCH_2CH_2)_2NH\cdot Br_2$, 36.2%]. From 0.2 g. of this addition product was obtained 0.1 g. of II·HBr; m. p. 169~170°C (from alcohol).

Anal. Found: C, 59.84; H, 5.68; N, 4.08. Calcd. for $C_{18}H_{20}O_2NBr$: C, 59.67; H, 5.56; N, 3.86%.

In the case of bromine addition product of base VI, the results were somewhat different from those of the above reaction. The bromine addition product of base VI, which was obtained from 5.0 g. of VI·HCl, was suspended in ether, and an excess of dilute solution of sodium hydroxide was added to the suspension with shaking. The addition product turned somewhat pale-yellow, but it was hardly soluble in ether. The pale-yellow matter was filtered and dried; yield, 3.5 g. Its bromine content was 27.5%, which is lower than the theoretical value of ($C_6H_5COCH_2CH_2)_2NCH_3\cdot Br_2$ (35.1%), and higher than that of VI·HBr (21.2%). Two grams of the above matter was dissolved in 50 ml. of alcohol and refluxed for one hour to give 1.4 g. of VI·HBr; m. p. 188~189°C (from alcohol). The mother liquor was slightly condensed to give an additional amount (0.2 g.) of VI·HBr.

Anal. Found: C, 60.65; H, 6.03; N, 3.79. Calcd. for $C_{19}H_{22}O_2NBr$: C, 60.64; H, 5.89; N, 3.72%.

The above crystals were converted into VI·HCl by repeated recrystallization from alcoholic hydrogen chloride; m. p. and mixed m. p. 169~170°C.

The ether layer, which was separated from the bromine addition product, was kept at room temperature to give the same product VI·HBr; m. p. 188~189°C; yield, 0.1 g.

Anal. Found: C, 60.36; H, 6.14; N, 3.89. Calcd. for $C_{19}H_{22}O_2NBr$: C, 60.64; H, 5.89; N, 3.72%.

Reaction of Bis-(β-benzoylethyl)-amine Hydrochloride (II·HCl) with Sodium Hypobromite.—One gram of II·HCl was added to 100 ml. of water. To this solution was added a solution of sodium hypobromite which was prepared by adding excessive sodium hydroxide to bromine water. The free base produced was extracted with ether. The ether solution was left to stand to produce crystals; yield, 1.0 g. The crystals were recrystallized from alcohol giving II·HBr; m. p. 170°C.

Anal. Found: C, 59.96; H, 5.65; N, 3.76. Calcd. for $C_{18}H_{20}O_2NBr$: C, 59.67; H, 5.56; N, 3.86%.

Summary

i) The addition of bromine to β-benzoylethylamine hydrochloride was studied. It was concluded that bromine molecule was added to β-benzoylethylamine hydrochloride in the form linking astride to the carbionium ion and the lone pair of electrons of the nitrogen atom, both of which were formed by prototropy.

ii) The bromine addition product of β-benzoylethylamine hydrochloride was treated with alkali for a little while to give *N*-bromo-β-benzoylethylamine which was very unstable and decomposed to give β-benzoylethylamine hydrobromide.

The author is particularly indebted to the late Professor Ryuzaburo Nozu and to Professor Ryozo Goto for their discussions and encouragement throught this investigation, and also to Professor Seishi Machida for his encouragement.

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Selective Reduction of Phosphatides with Lithium Aluminum Hydride. I. Ovolecithin

By Chieko URAKAMI, Hirochika OKURA and Mitsuko OKADA

(Received May 19, 1959)

For determination of the structures and the configurations of phosphatides, the following two methods were available. Long and Magure[1] carried out the reactions to derive L-α-glycerylphosphoric acid as described below:

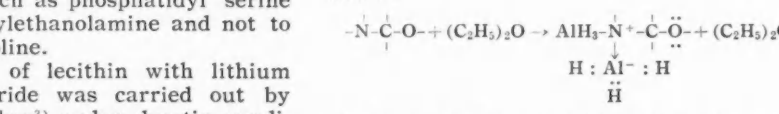
L-α-Lecithin —(Phospholipase C)→ 1,2-Diglyceride
—(Phosphorylation)→ L-α-Phosphatidic acid
—(Hydrolysis)→ L-α-Glycerylphosphoric acid

Baer and Maurukas[2] devised the so-called "diazometholysis" giving the phosphatidic acid dimethyl ester. In both methods, unsaturated fatty acids, if present, should be hydrogenated before carrying out these reactions. These two methods are, however, not always convenient for general application. The former is far more complicated and would require a sufficient amount of purified phosphatides for analysis of the final product. The latter is, on the other hand, simpler, but it is applicable to those containing the free amino group such as phosphatidyl serine and phosphatidylethanolamine and not to phosphatidylcholine.

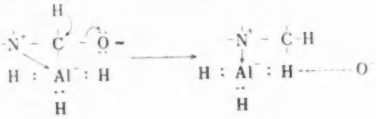
The reaction of lecithin with lithium aluminum hydride was carried out by Karrer and Jucker[3] under drastic conditions, at the boiling point of ether. Inorganic phosphorus, phosphine, glycerol and a substance with an amine-like odor were reported to be present in the reaction mixture. Apparently, all ester linkages of the lecithin molecule were cleaved. A number of instances of selective reduction by this reagent were reported, e. g. methyl 4-nitrovalerate was reduced to the corresponding alcohol at −35°C in 20 min., the nitro group being unattacked[4]. A selective reduction similar to this example may possibly be achieved with lecithin under carefully controlled conditions.

1) C. Long and M. F. Magure, *Biochem. J.*, **57**, 223 (1954).
2) E. Baer and J. Maurukas, *J. Biol. Chem.*, **212**, 39 (1955).
3) P. Karrer and E. Jucker, *Helv. Chim. Acta*, **35**, 1586 (1952).
4) H. Feuer and T. J. Kucera, *J. Am. Chem. Soc.*, **77**, 5740 (1955).

The authors' attention was focused on an ionic character of the coordinate covalences of the sulfonyl, nitro and phosphoryl groups. Under mild conditions approach of a hydride ion of lithium aluminum hydride present in ether solution to these groups may encounter some difficulty due to the presence of negatively charged oxygen atoms which are stabilized by resonance. If this plays a part in reduction of the lecithin molecule, the cleavage of the two fatty acid ester linkages would be easier than that of the two ester linkages of the phosphoryl group. However, the nitrogen atom of the choline may also play a role since Trevoy and Brown[5] showed the reaction to be a bimolecular nucleophilic substitution by a hydride ion and Gaylord[6] proposed a mechanism for the reduction of an –N–C–O– group, utilizing the ionic species, $AlH_4^- \rightleftharpoons AlH_3 + H^-$, and the concept of ether participation which have been proposed by Paddock[7], as shown below:

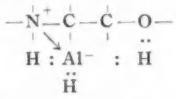


The coordination of AlH_3 with the lone pair on nitrogen can occur in the initial step. By analogy with Grignard reaction, the formation of a five-membered quasi-ring is suggested. As the result, nitrogen would become deficient in electron and tend to withdraw electron from the adjacent carbon giving the latter a positive character. The hydride ion could then displace the ethereal oxygen resulting in cleavage of the C–O bond:



5) L. W. Trevoy and W. G. Brown, ibid., **71**, 1675 (1949).
6) N. G. Gaylord, *Experientia*, **10**, 351 (1954).
7) N. L. Paddock, *Nature*, **167**, 1070 (1951).

This mechanism can possibly be applied to the choline moiety of the lecithin molecule, as far as the formation of a six-membered quasi-ring is concerned:



However, an electrostatic effect on the β-carbon atom would be not as strong as that on the α-carbon. The nitrogen atom in this case is already in the cationic form and has no lone pair available for coordination with AlH_3 but approach of AlH_4^- would be possible, resulting perhaps in a complex formation*. This may also encounter some difficulty, particularly at low temperatures at which the molecule exists in its ground state, because a hydride ion must overcome zwitterionic and possibly steric effects of the trimethyl group in its approach to the cationic nitrogen. Thus, a higher amount of energy would be required for the cleavage of the phosphoryl-choline linkage than that for the cleavage of the fatty acid ester linkage where no such obstacle exists.

By similar qualitative examination the following speculations may be made on relative ease of cleavage of the two phosphoryl ester linkages. The cleavage of the phosphoryl-glyceryl linkage depends on an attack by a hydride ion on the phosphoryl group only. On the other hand, in the cleavage of the phosphoryl-choline linkage a mechanism involving nitrogen may also participate; this may operate independently of the mechanism involving the phosphoryl group or assist the latter by making oxygen somewhat deficient in electron as a result of the formation of a six-membered quasi-ring. Accordingly the phosphoryl-choline linkage is considered to be cleaved somewhat more readily than the linkage between the phosphoryl and glycerol.

Thus, a step-wise cleavage of the lecithin molecule may be possible, i.e. the cleavage of the fatty acid ester linkages, giving the corresponding alcohols and glycerylphosphorylcholine (with retention of the configuration); or the cleavage of the choline moiety, following the removal of the fatty acids, giving choline and a reduced form of glycerylphosphoric acid**. Accordingly, attempts were made to find suitable reaction conditions to achieve either one of the two possibilities by controlling temperature, time and amounts of lithium aluminum hydride.

* The authors used "AlH_3" in a preliminary report on this subject, This Bulletin, **31**, 779 (1958), but presently consider that it must be reserved as such.

Experimental

Materials.—*Lecithin.*—Crude egg yolk lecithin was purified according to Hanahan's method[8], (P : N, 1 : 1.10 and 15.8% choline).

DL-α-Glycerylphosphorylcholine.—This compound was synthesized according to the method of Baer and Kates[9], (α-glyceryl ester: choline, 1.03 : 1.0).

Analytical Methods.—*Choline.*—Choline in glycerylphosphorylcholine was determined by Schmidt's method[10] and in lecithin by Glick's method[11].

Phosphorus.—The conventional method of wet incineration, with 10 N sulfuric acid and hydrogen peroxide, was used to convert organic phosphorus to the orthophosphate. The inorganic phosphate was then determined spectrophotometrically according to the method described by Burmaster[12] or by Ernester et al.[13] Concentrations of the reagents were altered, however, as circumstances required.

Ester.—The method described by Bauer and Hirsch[14] was employed.

α-Glycol.—The periodate oxidation method of Voris et al.[15] was used.

Reaction of Lecithin with Lithium Aluminum Hydride.—One hundred milligrams of lithium aluminum hydride was dissolved in 50~60 ml. of dry ether (0.1~0.2% solution). The solution was filtered first through glass wool packed in a glass tubing of about 6 mm. in diameter and then through a sintered glass filter sealed in a glass tubing of about the same diameter and transferred into a specially constructed burette. The filtration and transfer were carried out by applying pressure with dry nitrogen gas. Calcium chloride tubes were provided to keep the entire system in a dry state. A flask of about 100 ml. capacity containing a cooled ether solution of lecithin was attached to the burette and a calculated amount of the reducing agent*** was added in small portions so that the temperature

** A trivalent phosphorus compound may be formed as a result of an attack of AlH_4^- on the positively charged phosphorus atom. This sort of interaction was shown to occur under drastic conditions (the formation of phosphine was recognized)[31] and it may be possible that even under mild conditions this may occur to a certain extent.

8) D. J. Hanahan et al., *J. Biol. Chem.*, **192**, 623 (1951).
9) E. Baer and M. Kates, *J. Am. Chem. Soc.*, **70**, 1394 (1948).
10) G. Schmidt et al., *J. Biol. Chem.*, **197**, 601 (1952).
11) D. Glick, ibid., **156**, 643 (1944).
12) C. F. Burmaster, ibid., **164**, 233 (1946).
13) L. Ernester et al., *Acta Chem. Scand.*, **4**, 942 (1950).
14) F. C. Bauer, Jr. and E. F. Hirsch, *Arch. Biochem.*, **20**, 242 (1949).
15) L. Voris et al., *J. Biol. Chem.*, **133**, 491 (1940).

*** Concentrations of the ether solution were determined from time to time by the conventional method of hydrogen gas liberation. Aliquots were delivered from the burette.

of the reaction mixture could be maintained constant. Stirring with the magnetic stirrer was continued for a desired length of time. The reaction mixture was cooled and decomposed with wet ether. A sufficient amount of water was added to separate the organic layer. The aqueous phase was shaken twice with a small portion of fresh ether and the ether extracts were combined. The aqueous layer was then washed with chloroform to remove lysolecithin (this step was omitted in later experiments since no lysolecithin was found to be present in the chloroform extract). The ether extract was made up to a known volume, usually 25 ml., and aliquots were taken for analyses of organic phosphorus and esters. The aqueous phase was made acid with 10 N sulfuric acid to dissolve the precipitate, the solution filtered and made up to a known volume, usually 50 ml., for analyses of inorganic phosphorus, total phosphorus, free choline and total choline.

Isolation of L-α-Glycerylphosphorylcholine. — Lecithin (about 400 mg.) was reduced under the optimum conditions (14°C, Table V). After decomposing the reaction mixture with water, the precipitate formed was removed by centrifugation. The clear solution was passed through a column of IRC-50 and the eluate was analyzed for choline and α-glycol (α-glycol: choline, 1.02: 1.00). The eluate was then concentrated under reduced pressure in the atmosphere of nitrogen and the amorphous cadmium chloride addition complex was prepared according to the procedure described by Baer[9] (Found: P, 5.24%). A solution of the complex was passed through a mixture of 4 ml. of Dowex 3 and 2 ml. of IRC-50 and the solution analyzed for α-glycol, total P and choline (Found: α-glycol : P : choline, 0.97 : 1.00 : 1.02). α-Glycerylphosphorylcholine recovered after passing the resin column was found to be 94%. The crystalline cadmium chloride complex was prepared and analyzed (Found: C, 21.56; H, 4.80) after drying over phosphorus pentoxide at 56°C for 8 hr. under 3 mmHg. The infrared spectrum of this compound was found to be identical with that of the synthetic DL-α-glycerylphosphorylcholine. Its optical rotation was determined on the concentrate of the aqueous solution freshly prepared by repeating the reduction and purification in the same manner as described above [Found: $[\alpha]_D^{24}-2.96\pm0.2°$ (c, 2.2 water); $[\alpha]_D^{25}-2.85\pm0.1°$ (Baer)].

Preliminary experiments with α- and β-glycerylphosphoric acids in the same manner as described for the reduction of lecithin showed that no migration of the phosphoryl group occurred. Similar experiments with glycerylphosphorylcholine was not possible due to technical dfficulties. The migration of the phosphorylcholine groups is, however, unlikely to occur under such mild reaction conditions.

Results and Discussion

The results shown in Tables I and II indicate that the reaction proceeds through

TABLE I. REDUCTIVE CLEAVAGE OF OVOLECITHIN WITH LITHIUM ALUMINUM HYDRIDE AT 20°C: 15 mol. OF $LiAlH_4$ PER MOLE OF LECITHIN*

Reaction time (hr.)	3	5
Sample wt. (mg.)	201	86
Ch. in sample (mg.)	31.8±0.3	13.9±0.0
Total Ch. (mg.) in aq. phase	31.8±0.6	11.7±0.01
Free Ch. (mg.) in aq. phase	27.7±0.3 (87)	11.3±0.2 (81)
Inorganic P (mg.) in aq. phase	0.72±0.00 (9)	0.56±0.04 (16)
Organic P (mg.) in ether phase	0.00	0.00
Organic P (mg.) in chloroform extract	0.00	0.00

* For the calculation of the mole ratio 778 was used as an average molecular weight of lecithin. Ch. stands for choline. The figures in parentheses are percentages based on an amount of choline or phosphorus present in each sample weight.

TABLE II. REDUCTIVE CLEAVAGE OF OVOLECITHIN WITH LITHIUM ALUMINUM HYDRIDE AT 20°C: 3 mol. OF $LiAlH_4$ PER MOLE OF LECITHIN

Reaction time (hr.)	3	5	10
Sample wt. (mg.)	86	113	113
Ch. in sample (mg.)	13.9 ±0.0	17.8[a]	17.8[a]
Total Ch. (mg.) in aq. phase	13.9 ±0.0	19.6±0.5	15.7±0.3
Free Ch. (mg.) in aq. phase	5.65±0.2 (41)	11.3±0.2 (64)	12.3±0·3 (69)
P in sample (mg.)[a]	3.42	4.52	4.52
Inorganic P (mg.) in aq. phase	0.00	0.13 (3)	0.13 (3)
Total P (mg.) in aq. phase	2.12±0.01 (62)	2.88±0.11 (64)	3.06±0.1 (68)
Total P in ether phase	0.00	0.00	0.00
Total P in chloroform extract	0.00	0.00	0.00

Ch. stands for choline. The figures in parentheses are percentages based on an amount of choline or phosphorus present in each sample weight.

a) Calculated values.

TABLE III. REDUCTIVE CLEAVAGE OF OVOLECITHIN WITH LITHIUM ALUMINUM HYDRIDE AT 18°C: 2 mol. OF $LiAlH_4$ PER MOLE OF LECITHIN

Reaction time (min.)	5	5	10
Sample wt. (mg.)	100	120	120
Ch. in sample (mg.)	15.3 ±0.3	19.3±0.3	19.3±0.3
Total Ch. (mg.) in aq. phase	13.1 ±0.1	12.1±0.4	20.4±0.0
Free Ch. (mg.) in aq. phase	3.01±0.1 (19)	2.1±0.2 (11)	6.4±0.2 (33)

Ch. stands for choline. Those figures in parentheses are percentages based on the choline content of the sample.

TABLE IV. REDUCTIVE CLEAVAGE OF OVOLECITHIN WITH LITHIUM ALUMINUM HYDRIDE AT 16°C: 2 mol. OF $LiAlH_4$ PER MOLE OF LECITHIN

Reaction time (min.)	30	60
Sample wt. (mg.)	113	113
Ch. in sample (mg.), calcd.	17.8	17.8
Total Ch. (mg.) in aq. phase	19.1±0.9	19.6±0.5
Free Ch. (mg.) in aq. phase	4.1±0.2 (23)	4.4±0.2 (25)
P in sample (mg.), calcd.	4.52	4.52
Total P (mg.) in aq. phase	3.56±0.0 (79)	3.31±0.2 (73)
Total P (mg.) in ether phase	0.02	0.00
Total P (mg.) in chloroform extract	0.02	0.00

Ch. stands for choline. Those figures in parentheses are percentages based on an amount of choline or phosphorus present in each sample taken.

TABLE V. REDUCTIVE CLEAVAGE OF OVOLECITHIN WITH LITHIUM ALUMINUM HYDRIDE 2 mol. OF $LiAlH_4$ PER MOLE OF LECITHIN

Temperature (°C)	14	10	10
Reaction time (min.)	10	20	20
Sample wt. (mg.)	120	160.9*	128.6*
Ch. in sample (mg.)	19.1±0.3	22.7[a)]	18.1[a)]
Total Ch. (mg.) in aq. phase	18.0±0.1	23.6±0.1	18.3±0.0
Free Ch. (mg.) in aq. phase	0.8±0.1 (4)	0.0	0.0
P in sample (mg.), calcd.	4.78	6.82	5.45
Total P (mg.) in aq. phase	4.00±0.06	7.03±0.07	5.40±0.03
Total P (mg.) in ether phase	0.02±0.00	0.04±0.00	0.05±0.00
Ester (m. e.), calcd.		0.444	0.355
Ester (m. e.) in ether phase		0.004±0.002 (0.9)	0.004±0.001 (1.12)

* The sample of lecithin employed was prepared by the method of Rhodes and Lea, *Biochem. J.*, **65**, 526 (1957), and its analytical results were; choline : P : ester, 1 : 1.17 : 2.50.

a) Calculated values based on the analytical results.

Ch. stands for choline and m. e. for milliequivalent. The figures in parentheses are percentages based on choline or ester content of each sample taken.

the formation of glycerylphosphorylcholine and not phosphorylcholine, since choline containing substances in the aqueous phase release the total amounts of choline present in the samples on acid hydrolysis. Therefore, the experiments under much milder conditions were carried out so that only glycerylphosphorylcholine would be produced. These results are shown in Tables III—V.

It was of interest to see if ether insoluble glycerylphosphorylcholine itself would release the choline moiety by lithium aluminum hydride in ether, the synthetic glycerylphosphorylcholine was, therefore, reacted at 20°C for 3 hr. with 15 mol. of lithium aluminum hydride per mole of the compound. It was found that about 21% free choline was released.

From the results shown in Tables III—V,

the optimum conditions for the reductive cleavage of lecithin giving a 100% yield of glycerylphosphorylcholine appears to be 20 min. at 10°C with a mole ratio of lecithin to lithium aluminum hydride 1 : 2 (Table V). Some phosphorus and ester were found to be present in the ether phase, but this is considered to be due to some impurities present in the sample employed as indicated by its analytical results. According to its optical rotation observed, the glycerylphosphorylcholine formed in the reaction has the L-α-configuration. This method is, therefore, not only simple for the determination of configurations of lecithin, but also a useful method for the preparation of L-α-glycerylphosphorylcholine.

Tables III and V show that the reaction involving the release of the choline moiety is quite sensitive to temperature. With the temperature difference of only four degrees, 18, 14 and 10°C, amounts of choline released decrease from 30 to 4% and finally to 0%, respectively. On the other hand, it is not affected much by reaction time as shown in Tables III, IV and II. It appears then that temperature must be raised higher than 20°C for a complete release of the choline moiety as shown in Table I. The fact that the reaction is sensitive to temperature would mean that an amount of energy required for the cleavage of the phosphoryl-choline linkage is significantly higher than that required for the cleavage of the fatty acid ester linkage. It is quite in accord with what the authors have anticipated.

In those cases where considerable amounts of choline are formed, the total amounts of phosphorus recovered in the aqueous phase are only 62~68% of the calculated amounts (Table II), despite the absence of phosphorus in the organic phase. It is also noticed in the same table that the amounts of the inorganic phosphorus in the aqueous phase are not equivalent to that of the choline moiety released; only 0~3% of the inorganic phosphorus are detected where 41~69% free choline are formed. These results may indicate that some complex mechanisms are involved in the cleavage of the choline moiety.

If a mechanism similar to that proposed by Gaylord[5] operates in the cleavage of the choline moiety, trimethylethylamine should be formed. If, on the other hand, a mechanism involving the phosphoryl moiety participates, choline and a reduced form of α-glycerylphosphoric acid, which may not be detected by the method of analysis employed must be produced. In Table IV, 79 and 73% of phosphorus found in the aqueous phase can be considered to have been derived from 77 and 75% of glycerylphosphorylcholine, respectively. Therefore, 21 and 27% of undetected phosphorus may be ascribed to a reduced form of glycerylphosphoric acid, indicating that the latter mechanism may have played a role. Under such mild conditions, liberation of phosphine would not be possible, for an amount of lithium aluminum hydride used is far less than that required for reduction of the phosphoryl group to its ultimate stage. When three moles of the reducing agent is used (Table II), of 62% total phosphorus detected in the aqueous phase after three hours of reaction time 59% can be accounted for glycerylphosphorylcholine and the remaining 3% may have come from glycerylphosphoric acid (since no inorganic phosphorus is found to be present). Similarly, with 5 and 10 hr. of reaction time 25 and 34%, respectively, may have been derived from glycerylphosphoric acid. Undetected phosphorus would then amount to 38, 36 and 32% for 3, 5 and 10 hr., respectively, of the reaction time in these instances. Therefore, under these conditions, the two mechanisms mentioned above appear to have participated simultaneously, though participation of the latter mechanism seems to predominate in the three hour run. This may indicate that energy requirements for the formation of an intermediary complex with the cationic nitrogen are somewhat higher than that with the phosphoryl group.

Suppose that the formation of the inorganic phosphate is the only indication available for the cleavage of the glycerylphosphoryl linkage, this ester linkage is considered to be the most stable one in the lecithin molecule against lithium aluminum hydride. It may also be pointed out that "free choline" given in the tables constitutes of a mixture of choline itself and the quarternary amine according to the foregoing discussions.

Summary

The optimum conditions for cleavage of the fatty acid ester linkages in the lecithin molecule were found to be 20 min. at 10°C with the use of two moles of lithium aluminum hydride per mole of lecithin.

The product formed under these conditions was identified to be L-α-glycerylphosphorylcholine when ovolecithin which was shown to be L-α-lecithin[8] was used.

Discussion has been presented as to two mechanisms possibly participating in the cleavage of glycerylphosphorylcholine, one involving a complex formation with the phosphoryl group and the other with the cationic nitrogen atom of the choline base.

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Electrode Kinetics of Indium(III) at the Dropping Mercury Electrode

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The polarographic behavior of indium(III) has been investigated in various media by many authors. In these investigations two typical electrode processes are noticeable: One is a reversible process which proceeds at about −0.5 V. vs. S. C. E. in the chloride, bromide, iodide or organic acid solution[1,2]. The other is an irreversible process which proceeds at about −1.0 V. vs. S. C. E. in the perchlorate[2] or phosphate[3] solution*. In this report is presented the evaluation of the rate constant of the irreversible electrode process of indium(III) in the perchlorate medium, and the temperature dependence of the rate constant is discussed.

Experimental

The apparatus used was described in the previous report[4] and was not modified in any detail.

All the reagents were of analytical grade. The stock solution of indium perchlorate was prepared by dissolving indium oxide (weighed as $In_2O_3 \cdot 3H_2O$) in perchloric acid. Indium oxide was prepared from indium chloride by precipitating indium hydroxide with ammonium hydroxide and by desiccating the precipitate to a constant weight at 130°C.

In order to avoid the overlap of the hydrogen wave on the indium wave, the hydrogen-ion concentration was controlled by adding sodium hydroxide. The concentration of the perchlorate ion in the test solution was 0.5 F.

Purified nitrogen was bubbled to remove dissolved oxygen in the test solution prior to submission to polarography.

The temperature was kept constant within the change of ±0.1°C by a thermostat.

Results and Discussion

Irreversible Current-Voltage Curve of Indium(III).—The irreversible current-voltage curve of indium(III) in the perchlorate medium is illustrated in Fig. 1. Usually, this irreversible wave is accompanied by a pronounced maximum of the first kind. This maximum wave can be suppressed by the addition of a surface active material such as gelatine, methyl red or methyl cellulose. The adsorption of the surface active material on the surface of the dropping mercury electrode (DME), however, seems to change the potential distribution on and near the electrode surface, and this effect results in the variation of the transfer coefficient[3,5]. Moreover, the adsorptive concentration will vary with the change of temperature. Accordingly, the use of a surface active material is not desirable for the purpose of investigating

1) J. Heyrovsky, *Chem. Listy*, **19**, 168 (1925); S. Takagi, *J. Chem. Soc. London*, 301 (1928); J. Tomes, *Collection Czechoslov. Chem. Communs.*, **9**, 12 (1937); J. A. Schufle, M. F. Stubbs and R. Witman, *J. Am. Chem. Soc.*, **73**, 1013 (1951); Z. S. Mukhina, *Zavodskaya Lab.*, **14**, 354 (1948); G. Reinacher and E. Hoschek, *Z. anorg. u. allgem. Chem.*, **268**, 260 (1952); F. Ensslin, *Metall u. Frg.*, **38**, 305 (1941), *Chem. Abstr.*, **36**, 6107 (1942); M. Bulovova, *Collection Czechoslov. Chem. Communs.*, **19**, 1123 (1954).

2) J. J. Lingane, *J. Am. Chem. Soc.*, **61**, 2099 (1939).

3) H. Imai, *J. Sci. Hiroshima Univ.*, **A22**, 291 (1958).

* H. Nakatani has reported that both of the two electrode processes can be observed in one polarogram in the acetic acid—ammonium acetate buffer, and that the second wave is more pronounced with the addition of gelatine [*J. Sci. Hiroshima Univ.*, **A19**, 183 (1955); ibid., **A20**, 49 (1956)].

4) H. Imai, This Bulletin, **30**, 873 (1957).

5) P. Delahay and J. E. Strassner, *J. Am. Chem. Soc.*, **73**, 5219 (1951); H. Imai and S. Chaki, This Bulletin, **29**, 498 (1956).

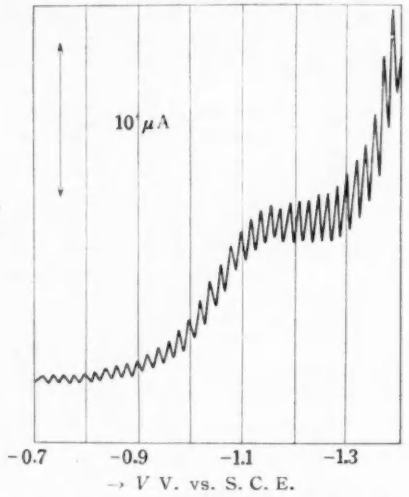

Fig. 1. The current-voltage curve of indium(III) in 0.5 F perchlorate.
Temp.=20°C, m=1.8$_1$, t=4.9$_0$ (open circuit), [In^{3+}]=1 mF.

the temperature dependence of the reaction rate. In this experiment, the lifetime of the DME was elongated by lowering the mercury head, and the supporting electrolyte was appreciably concentrated. Under these conditions, the maximum wave could be satisfactorily minimized. The test solution may be contaminated by the trace of surface active materials which have been accidentally intermixed. After this trace was removed by adding active charcoal, the maximum could not be suppressed in any way. The presence of this trace, however, scarcely affects the value of the transfer coefficient in the temperature range examined, as is illustrated in Table I.

When the hydrogen-ion concentration was too small, the test solution became turbid owing to the formation of indium hydroxide. Even when perchloric acid was added until the turbidity had just disappeared, the current-voltage curve of indium was too greatly extended, from −0.5 to −1.3 V. vs. S. C. E. On the other hand, when the acidity was too great, the hydrogen wave overlapped on the indium wave in question. Therefore, the perchloric acid concentration as great as 0.04 F was preferable.

Evaluation of Diffusion Constant. — The value of the diffusion constant of the indium ion is required for the calculation of the rate constant. This value was evaluated from the diffusion-controlled limiting current by Ilkovic's equation, i. e.

$$D^{1/2}=i_d/607\,nCm^{2/3}t^{1/6} \qquad (1)$$

where D is the diffusion constant in cm^2/sec., i_d is the mean diffusion-controlled current in μA, n is the number of electrons transferred per an ion, C is the bulk concentration of indium(III) in mF, m is the average mass of mercury flowing in mg./sec. and t is the life-time of the DME in sec. The evaluation of the number of electrons transferred per an ion was carried out as follows: When chloride, iodide or acetate was added to the test solution, the irreversible wave was changed to the reversible one, the half-wave potential being simultaneously changed from −1.0 to −0.5 V. vs. S. C. E. It was confirmed that the diffusion-current constants of the two waves were practically equal[5]. In the reversible electrode process the value of n was evaluated to be three from the inclination of the $\log[i/(i_d-i)]$ versus E (the potential of the DME) plot. Accordingly, the value of n in the irreversible electrode process will also be three. The evaluated value of the diffusion constant is given in Table I.

Evaluation of Transfer Coefficient and Rate Constant.—The value of $\log[i/(i_d-i)]$ was plotted versus the potential of the DME from the irreversible current-voltage curve. This polt gave a straight line near the half-wave potential. According to Matsuda and Ayabe's theory[6], the inclination of the linear portion of this plot is a function of the transfer coefficient as is given in Eq. 2, i. e.

$$E=\frac{RT}{\alpha nF}\{2.3\log(k_f^\circ f^\circ t^{1/2}D^{-1/2}) -0.12-2.2\log[i/(i_d-i)]\} \qquad (2)$$

where f° is the activity coefficient of the depolarizer in the solution and the other symbols are used with their usual significance. The evaluated value of αn, which is the product of the transfer coefficient by the number of electrons involved in the rate-determining reaction, is illustrated in Table I.

The rate constant, k_f°, referred to 0 V. vs. N. H. E. was evaluated from Eq. 3[6], i. e.

$$E_{1/2}=\frac{RT}{\alpha nF}[2.3\log(k_f^\circ f^\circ D^{-1/2}) +1.15\log t-0.12] \qquad (3)$$

6) H. Matsuda and Y. Ayabe, This Bulletin, **28**, 422 (1955).

where $E_{1/2}$ is the half-wave potential of the irreversible wave in volts vs. N. H. E. The values of the rate constant at various temperatures ranging from 20 to 30°C are illustrated in Table I.

TABLE I. THE DIFFUSION CONSTANT, THE TRANSFER COEFFICIENT AND THE RATE CONSTANT OF THE ELECTRODE PROCESS OF INDIUM-(III) IN 0.5 F PERCHLORATE

Temperature T°K	Diffusion constant D, cm²/sec.	Transfer coefficient αn	Rate constant k_f°, cm./sec.
293.2	8.0×10^{-6}	0.66	2.2×10^{-12}
299.7	9.6×10^{-6}	0.66	4.7×10^{-12}
303.2	10.8×10^{-6}	0.65	7.3×10^{-12}

Temperature Dependence of Rate Constant.— From Table I, the logarithm of the rate constant was plotted versus the reciprocal of the absolute temperature. This plot is satisfactorily linear as is illustrated in Fig. 2. From the inclination of this plot, the heat of activation at constant pressure (ΔH^*) was calculated by Arrhenius's equation, i. e.

$$\mathrm{d}\ln k_f^\circ/\mathrm{d}t = \Delta H^*/RT^2 \quad \text{or}$$

$$\log k_f^\circ = c - \Delta H^*/2.3\,RT \qquad (4)$$

where c is a constant. The heat of activation at constant volume (ΔH^+) was calculated by Eq. 5 in order to apply the absolute rate expression.

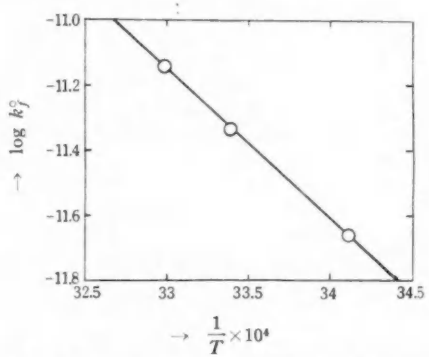

Fig. 2. The temperature dependence of the rate constant of the electrode process of indium(III) in 0.5 F perchlorate.

TABLE II. THE HEAT OF ACTIVATION IN THE ELECTRODE PROCESS OF INDIUM(III) IN 0.5 F PERCHLORATE

The heat of activation at constant pressure ΔH^*, kcal./mol.	The heat of activation at constant volume ΔH^+, kcal./mol.
21.1	20.5

$$\Delta H^* = \Delta H^+ + RT \qquad (5)$$

These data are illustrated in Table II.

On applying the absolute rate theory to an electrode process, it is noteworthy that the applied potential plays a role as the activation energy of the electron transfer, and that the electrode reaction is a heterogeneous reaction. It is well known that a spontaneous potential difference exists at the mercury-solution interface. Accordingly, the value of the applied potential as the activation energy must be referred to the zero-charge potential, i. e. the Lippmann-potential. Delahay[7] has given a modified expression of the absolute rate theory for an electrode reaction which involves no kinetic complication, as is given in Eq. 6, i. e.

$$k_f^\circ = \frac{ekT}{h}\cdot\rho\cdot\exp(-\Delta H^+/RT) \times\exp(\alpha nFE_m/RT)\cdot\exp(\Delta S^+/R) \qquad (6)$$

where e is the transmission coefficient, k is the Boltzmann constant, h is the Planck constant, ρ is an arbitrary factor in cm., E_m is the Lippmann potential referred to N. H. E.** and ΔS^+ is the entropy of activation in e. u. Eq. 6 involves two arbitrary factors. One of them is the transmission coefficient, the value of which was assumed to be 1 in this calculation. The other arbitrary factor is ρ, which was introduced to equalize the dimension of the right side of Eq. 6 to the dimension of the rate constant (cm./sec.).

Delahay has proposed a value as great as that of 2.0×10^{-8} cm. as the mean distance between two depolarizer ions in the bulk solution. It is noteworthy that this value is of the order of the atomic radius. Supposing that the depolarizer at the vicinity of the electrode surface pertains to the rate of the electrode reaction, the above mentioned value of ρ seems to be impossibly small. Accordingly, the value of ρ was evaluated from the depolarizer concentration at the vicinity of the electrode surface. The value amounts to 5.7×10^{-6} cm. as the mean interionic distance between the two depolarizer ions at the vicinity of the electrode surface.

The transmission coefficient does not

7) P. Delahay, *J. Am. Chem. Soc.*, **75**, 1190 (1953); "New Instrumental Methods in Electrochemistry", Interscience Publishers, Inc. New York (1954), p. 41.

** The Lippmann-potential of the DME in 0.5 F perchlorate was evaluated by the "VDME" method[8] as great as -0.23_7 V. vs. N. H. E.

8) H. Imai, S. Inouye and S. Chaki, This Bulletin, **31**, 767 (1958); ibid., **32**, 994 (1959).

inherently vary in the order of its magnitude, and accordingly, it does not seriously affect the value of the entropy of activation, while the possible variation of the order of ρ-value seriously affects the value of the entropy of activation. In Table III is presented the value of the entropy of activation evaluated in correspondence to the values of ρ as great as 5.7×10^{-6}.

TABLE III. THE ENTROPY OF ACTIVATION AND THE FREE ENERGY OF ACTIVATION IN THE ELECTRODE PROCESS OF INDIUM(III) IN 0.5 F PERCHLORATE

Arbitrary factor ρ, cm.	Entropy of activation S^*, e. u.	Free energy of activation F^*, kcal.
5.7×10^{-6}	−5.7	22.2

In the above mentioned case the entropy of activation is appreciably negative. Accordingly, it can be assumed that the randomness or disorder in the atomic arrangement of the activated state is less than that of the original state. Lingane[2] has reported that indium(III) is supposed to exist in the form of the aquo complex in the perchlorate solution. Hence, it can be concluded that, when the indium(III) aquo ion enters into the electric field of the electrode surface, the possible coordination of water dipols will be more or less deprived of its randomness prior to the electron transfer.

The reasonable evaluation of ρ-value is reserved for the future.

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Density Measurement in Dilute Aqueous Solution of Polyvinyl Alcohol

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Precise determination of solution density has an important bearing on the measurements of various physicochemical properties of high polymers in dilute solution. Fragmentary data can be found in literature, but the density measurement itself was scarcely ever chosen as the subject of studies on dilute high polymer solutions, except in the case of a few studies concerning polystyrene[1-5].

Recently a suggestion was made by Kobatake[6] on the possibility of elucidating the polymer-solvent interaction from the density data of dilute solution. According to an equation proposed by Kobatake[6], the polymer-solvent interaction B_{12} can be best estimated from the molecular weight dependence of the solution density. An analysis of Schulz and Hoffmann's data[5] on the apparent specific volume of polystyrene and polymethyl methacrylate was carried out by Kobatake and Inagaki[7] along with this line of approach. Some interesting data concerning molecular interactions in solution were obtained from the values of B_{12}. It would seem, therefore, that systematic accumulation of density data should contribute to the problems in dilute high polymer solutions.

In this paper, the density of an aqueous solution of polyvinyl alcohol (PVA) is measured by the use of well defined and fractionated samples, and some analysis

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1) D. J. Streeter and R. F. Boyer, *Ind. Eng. Chem.*, **43**, 1790 (1951).
2) W. Heller and A. C. Thompson, *J. Colloid Sci.*, **6**, 57 (1951).
3) B. Rosen, *J. Polymer Sci.*, **17**, 559 (1955).
4) A. Horth and M. Rinfret, *J. Am. Chem. Soc.*, **77**, 503 (1955).
5) G. V. Schulz and M. Hoffmann, *Makromol. Chem.*, **23**, 220 (1957).
6) Y. Kobatake, *Researches on Chemical Physics (Busseiron Kenkyu)*, **69**, 30 (1953).
7) Y. Kobatake and H. Inagaki, private communication.

of the results are made on the basis of Kobatake's equation[6,7].

In order to determine the solution density, the authors adopted the method of floating equilibria which is the same as that used for the quantitative analysis of heavy water concentration[8,9]. This method was proved to be applicable also to polymer solution. It was rather easy to obtain the solution density and polymer concentration with the same accuracy as that obtained by other methods[2,3,5].

Experimental

Preparation of Materials.—The PVA fractions were obtained by the saponification of polyvinyl acetates which were polymerized in solution under various conditions and fractionated in acetone-water system. Acetyl group content in the resulting PVA samples was less than 0.2%.

The molecular weight of PVA samples was determined from the intrinsic viscosity in water. The viscosity average molecular weight calculated from Nakajima's equation[10] is shown in Table I. In the same table, experimental conditions for polymerization are also tabulated since they have an important bearing on the molecular weight dependence of density.

Unfractionated samples of PVA were also used in the preliminary experiments.

Water as solvent was obtained by the careful distillations of conductivity water.

Apparatus and Float.—The apparatus used for the measurement of floating equilibria is based on the one described by Harada[9] for the quantitative analysis of heavy water. The float, made of silicate glass, is spindle-shaped and 2~3 cm. long. The upper spherical part of the float is hollowed, and the apparent specific weight of the whole float is adjusted to a value of the solvent density (water, in this case) near room temperature. The temperature at which the measurements run is always regulated within the accuracy of 0.005°C by a large outer thermostat.

The motion of the float in the sample liquids was followed by a traveling microscope and the equilibrium temperature of the float was read on a Beckmann thermometer.

Density Measurement. — *(a) Preparation of sample solution.* — The PVA samples, after the saponification, were purified by extraction with methanol in a Soxhlet extractor for three days or longer and dried in vacuo. These samples were dissolved into water in a flask which was placed on a boiling water bath for more than eight hours and about 1% solution was prepared. The solution was then filtered through the glass filters Nos. 2 and 4, and again heated on a boiling water bath. This stock solution was diluted by weight and/or by volume to obtain required concentrations and each solution was stored in a closed tube. Before use, each solution was kept overnight in a thermostat at 80°C. Concentrations of the solution were determined by evaporating the solvent and drying in vacuo at 60°C to constant weight.

(b) Measurement of equilibrium temperature.— The equilibrium temperature, T_0, of the float in water—the temperature which keeps the float both from sinking and floating—is first measured for each float. The "apparent density" of the float is next obtained by comparing this temperature with the density-temperature curve of water (chain-dotted line in Fig. 1). Thus, when the equilibrium temperature in solution, T, is again measured for each float of known density, the density-temperature curve of the solution (solid line in Fig. 1) is immediately obtained. The density of solution at any temperature is also determined from this curve.

In practice, the sensitivity of the float to

TABLE I. EXPERIMENTAL CONDITIONS IN POLYMERIZATION, FRACTIONATION AND MOLECULAR WEIGHT OF POLYVINYL ALCOHOL

	B-5	T-2	E-2	U-1	U-2	U-5
Polymerization						
Solvent	Benzene	Toluene	Ethanol			
Initiator	0.1% BPO	0.1% BPO	1.0% BPO			
Monomer, wt.%	60	60	30	Commercial sample		
Temp., °C	80	80	70			
Time, hr.	12	13.5	25			
Yield, %	74	44	60			
Fractionation						
Solvent/precipitant		Acetone/water				
Fractions	8	5	5	Unfractionated		
Temp., °C	25	25	25			
Molecular weight						
M_w ($\times 10^{-3}$)	70.4	24.2	8.4	107	96.8	57.2
P	1600	550	190	2430	2200	1300

8) T. W. Richards, J. H. Shipley and G. W. Harris, *J. Am. Chem. Soc.*, **34**, 599 (1912).
9) M. Harada, *J. Chem. Soc. Japan, Pure Chem. Sec. (Nippon Kagaku Zasshi)*, **56**, 811 (1935).
10) A. Nakajima and K. Furutati, *Chemistry of High Polymers (Kobunshi Kagaku)*, **6**, 460 (1949).

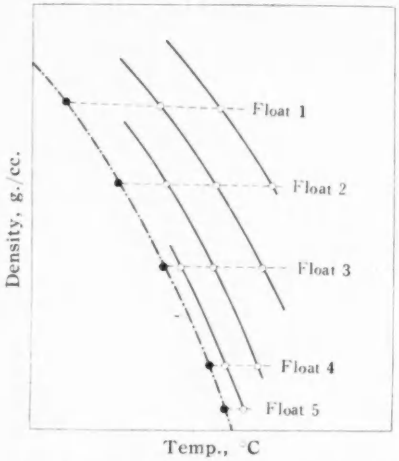

Fig. 1. The method of floating equilibria —— a schematic representation.
● T_0 in Eq. 2, ○ T in Eq. 2

temperature variation was higher than the constancy of the thermostat. The equilibrium temperature was then measured in the following two ways; namely, the "quasi-static" and the "dynamic" method[11]. In the former, floating equilibrium is determined directly by a fine adjustment of temperature, while the latter is based on the interpolation of the floating and sinking velocity of the float near the equilibrium temperature.

When the difference between the equilibrium temperature of the solution and that of the solvent is large, a correction for the thermal expansion of the float is required. In this case, the following equation was used,

$$d_t = d_0/(1+\alpha \cdot \Delta T) \quad (1)$$

$$\Delta T \equiv T - T_0 \quad (2)$$

where d_t and d_0 are the density of the float at T and T_0, respectively, and α is the coefficient of cubic expansion of silicate glass[12].

(c) *Apparent and partial specific volumes.*—Following the procedure given above, the solution density d_{12} can be obtained as a function of polymer concentration c_2 (g./cc.) and temperature. For the discussion of experimental data, however, it is convenient to use the apparent specific volume ϕ_2 (cc./g.) and the partial specific volume V_2 (cc./g.) of solute polymer in solution. They can be calculated from the solution density by the following equations,

$$\phi_2 = 1/d_1 - d_{sp}/c_2 \quad (3)$$

$$V_2 = \phi_2 + w_2(1-w_2)\cdot\partial\phi_2/\partial w_2 \quad (4)$$

$$V_2 \cong \phi_2 + c_2\cdot\partial\phi_2/\partial c_2$$

(for dilute aqueous solution) (5)

where d_1 is the density of solvent (g./cc.), w_2 is the weight fraction of solute polymer and $d_{sp} = (d_{12}-d_1)/d_1$.

Discussion of the Experimental Error.—Although the float is sensible to the temperature change of 0.001°C, fluctuation in excess of 0.003°C is inevitable in the determination of equilibrium temperature in both the two methods, quasi-static and dynamic. The error in the density determination, even when the work is very carefully done, is accordingly expected to be about $\pm 2\times 10^{-6}$. In practice, such a degree of precision was easily obtained in the measurement with water in which the "apparent density" of the float was quite stable.

While in PVA solutions, the "apparent density" of the float becomes somewhat unstable, though the cause is uncertain. PVA may be adsorbed to the float and sometimes an insoluble film may be formed on the surface. Under this circumstance, calibration with water is frequently required. Thus, the actual error found in PVA solution was not in excess of $\pm 4\times 10^{-6}$.

Finally, it was often observed that foam grows on the surface of the float and that the quasi-equilibrium of the float is attained especially in the measurement near 20°C. In the temperature region from 25 to 30°C with which the authors' experiment is concerned, however, the appearence of foam was rare and there was practically no experimental difficulty.

Results and Discussion

Equilibrium Temperature as Function of Polymer Concentration. — Fig. 2 shows the temperature difference (ΔT) vs. concentration relationship of PVA aqueous solution up to 1.0 g./100 ml. Each curve in the figure corresponds to the values obtained with using different floats. It is seen at once that the ΔT vs. concentration relationship can be regarded as almost linear below 0.5 g./100 ml., but convex in the more concentrated region. It can be also observed that the larger the "apparent density" of the float is (namely, the lower the T_0 of the float is), the more magnified the temperature difference is for the same sample solution. The molecular weight of PVA affects ΔT, though very minutely and can not be seen in the figure. This point will be discussed later.

The ΔT vs. concentration curve in Fig. 2 may be used as a calibration curve for the determination of polymer concentration in dilute solution. The temperature difference ΔT for PVA aqueous solution of 1.0 g./100 ml. reaches to about 9~10°C, while the equilibrium temperature itself can be obtained with a precision of 0.003°C. In this case, accordingly, a concentration difference of at least 0.003 g./100 ml. (i.e.

11) H. Akamatsu, *J. Chem. Soc. Japan (Nippon Kwagaku Kwaishi)*, **61**, 470 (1940).
12) G. W. Morey, "Properties of Glass", Reinhold Publishing Corp., New York (1954), p. 275.

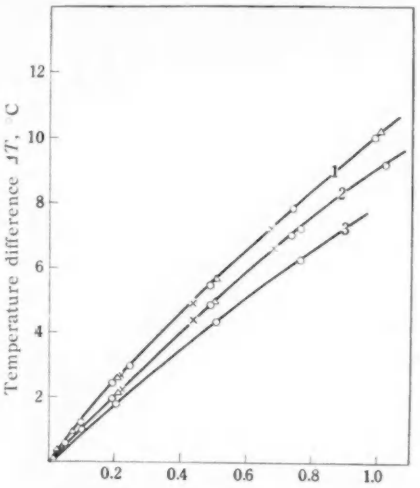

Fig. 2. Equilibrium temperature difference vs. polymer concentration relationship.
○ P=1300 × P=2200 △ P=2430
1 Float 6 (T_0=18.47°C)
2 Float 1 (T_0=21.29°C)
3 Float 9 (T_0=26.21°C)

0.003 wt. %) will be detectable by the present method.

Solution Density as Function of Polymer Concentration and Molecular Weight.—In Fig. 3, the solution density vs. polymer concentration relationship is shown for aqueous solution of fractionated PVA.

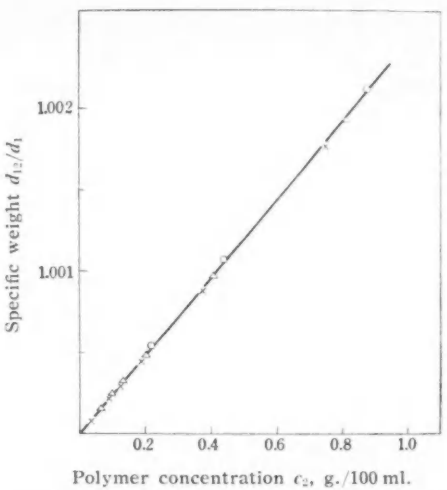

Fig. 3. Solution density vs. polymer concentration relationship for dilute solution of fractionated PVA at 30°C.
○ B-5 P=1600 △ T-2 P=550
× E-2 P=190

The data of d_{12}/d_1 (specific weight to solvent water) vs. c_2 fall on a straight line at least below the polymer concentration of 1.0 g./100 ml., and are slightly dependent on the molecular weight of PVA.

For a clear detection of this dependence, it is convenient to calculate the apparent specific volume ϕ_2 of PVA in solution. Fig. 4 shows the experimental values of

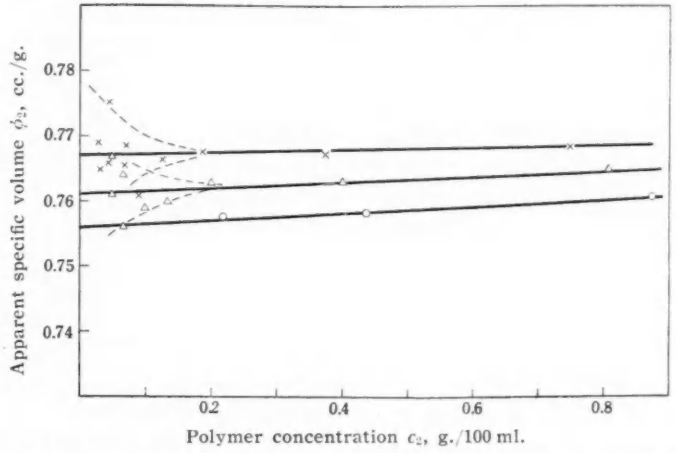

Fig. 4. Apparent specific volume of PVA in aqueous solution, as function of polymer concentration, c_2, at 30°C.
○ B-5 P=1600 △ T-2 P=550 × E-2 P=190

ϕ_2 calculated by Eq. 3 at each concentration. It is seen from the figure that ϕ_2 increases slightly with c_2 for every case concerned, though the data at extreme dilution are somewhat uncertain. It may be thus concluded that a negative second order term, though very small, does exist, if the d_{12} vs. c_2 relationship, as usual, is represented by a power series (see Eq. 6).

Another remarkable result seen on Fig. 4 is the clear dependence of ϕ_2 on the molecular weight of PVA. This dependence is expected from the simple qualitative consideration that the presence of the end-group which is different from the intermediate segment will affect the spatial configuration of the polymer molecule. It is seen that ϕ_2 decreases with increasing molecular weight, and the fifth decimal place of the solution density d_{12} is influenced by the molecular weight of the solute polymer. As is shown immediately after, ϕ_2 and the partial specific volume V_2 seem to be inversely proportional to the molecular weight of PVA. Taking this molecular weight dependence into account, the experimental formula for the solution density of a dilute solution of PVA at 30°C is proposed as follows:

$$\frac{d_{12}}{d_1} = 1+\left(0.249-\frac{2.47}{P}\right)\cdot c_2 -\left(0.64-\frac{88}{P}\right)\cdot c_2^2 \qquad (6)$$

where P is the polymerization degree of PVA and c_2 is the polymer concentration in g./cc. This equation could reproduce the experimental data very well.

Eq. 6 should prove useful for predicting the density of an aqueous solution of PVA, irrespective of the origins of the PVA samples, if the polymerization degree is not too low. However, it is to be remarked here that, if P is lower than 500, the solution density of PVA which is polymerized under different initiators may not be represented by this equation.

From Eq. 4 or 5, the partial specific volume V_2 of PVA is easily obtained. Because of scattering in the observed values of ϕ_2, the accurate determination of V_2 and its concentration dependence becomes difficult at concentrations lower than 0.2 g./100 ml., and V_2 only at the concentration of 0.5 g./100 ml. was estimated by interpolation. Plotting the experimental values of V_2 against $1/P$, a nearly linear relationship is obtained as in Fig. 5.

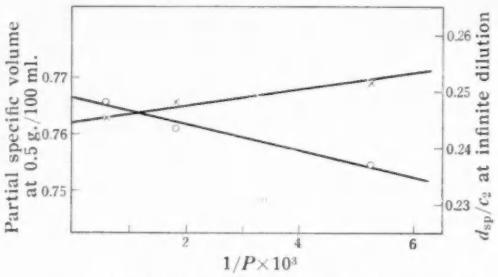

Fig. 5. Molecular weight dependence of $(d_{sp}/c_2)_{c_2\to0}$ and V_2 at 0.5 g./100 ml., at 30°C.
○ $\left(\frac{d_{sp}}{c_2}\right)_{c_2\to0}$ × V_2 at 0.5 g./100 ml.

In the same figure, the values of d_{sp}/c_2 at infinite dilution $(d_{sp}/c_2)_{c_2\to0}$ are also plotted against $1/P$. A linear relationship is observed here. This dependence of $(d_{sp}/c_2)_{c_2\to0}$ on P must be the same as that of $\phi_{2(c_2\to0)}$ as is easily seen from Eq. 3. Thus, one may write

$$\phi_2 = \phi_{2(P\to\infty)} + K/P \qquad (7)$$

at infinite dilution. Here, $\phi_{2(P\to\infty)}$ is the apparent specific volume of the polymer whose polymerization degree P is infinity and K is a constant.

Estimation of Polymer-Solvent Interaction.— If the end-segments in the polymer molecule are different in size from the intermediate segments, it is to be expected that ϕ_2 (or V_2) may change inversely proportional to the molecular weight of the polymer.

In fact, Kobatake[6] has derived theoretically an equation which is quite the same in form as Eq. 7. According to his theory, two constants in Eq. 7 can be correlated with the parameters of intermolecular potential as follows:

$$\phi_{2(P\to\infty)} = -\beta_{12}/m_2 \qquad (8)$$

$$K = -2\beta'_{12} + \frac{2\rho_1 B_{11}+1}{\rho_1} \qquad (9)$$

$$B_{12} = 2\beta'_{12} + P\beta_{12} \qquad (10)$$

where B_{11} is the excluded volume (or McMillan-Mayer's "irreducible integral"[13]) between two solvent molecules, B_{12} is the excluded volume between solvent- and polymer molecules, β_{12} is the excluded volume between solvent molecule and intermediate segment, β'_{12} is the excess excluded volume representing the end-group effect, m_2 is the molecular weight

13) W. G. McMillan, Jr. and J. E. Mayer, *J. Chem. Phys.*, **13**, 276 (1945).

TABLE II. EXPERIMENTAL VALUES OF APPARENT AND PARTIAL SPECIFIC VOLUMES AND POLYMER-SOLVENT EXCLUDED VOLUMES

P	$(d_{sp}/c_2)_{c_2\to 0}$	$\phi_{2(c_2\to 0)}$	V_2	$-B_{12}(\times 10^{-3})$	$-\beta_{12}$	$-\beta'_{12}$
1600	0.248	0.756	0.763	1.21		
550	0.243	0.761	0.766	0.415	0.755	1.20
190	0.237	0.767	0.769	0.143		

of monomer, and ρ_1 is the density (number density) of the solvent.

According to Orstein and Zernike[14], the B_{11} in Eq. 9 is correlated with the isothermal compressibility κ_1 as follows:

$$\frac{2\rho_1 B_{11}+1}{\rho_1} = kT\kappa_1 \qquad (11)$$

where k is the Boltzmann constant and T is the absolute temperature in °K. One can then calculate β_{12} and β'_{12} by Eqs. 8 and 9, and finally B_{12} by Eq. 10.

The authors will first estimate the second term $(2\rho_1 B_{11}+1)/\rho_1$ in Eq. 9. Using Eq. 11, the value of $(2\rho_1 B_{11}+1)/\rho_1$ for water is estimated to be 0.068 cc./g. from the experimental data of κ at ordinary pressure[15]. Thus, Eq. 9 can be reduced to

$$K = -2\beta'_{12}+0.068 \qquad (12)$$

Using the experimental results of $\phi_{2(c_2\to 0)}$ (extrapolated values of ϕ_2 to infinite dilution) and its molecular weight dependence, the authors calculate the values of β_{12}, β'_{12} and B_{12}, which are listed in Table II.

The value of β_{12} represents the "free volume" of PVA molecule per monomer unit, while β'_{12} is related to the excess contribution by end-segments. It may be concluded from the comparison between them that the contribution of the end-group in the polymer molecule to total interaction differs markedly from that of the intermediate segment and can not be neglected.

Furthermore, it is to be remarked here that a linear relationship between ϕ_2 and $1/P$ can also be expected from Eq. 9 even when the end-group effect is negligible. However, for the present case, β'_{12} have a large value in comparison with the second term in Eq. 9; the experimental value of K is estimated to be 2.47 cc./g., $-2\beta'_{12}$ is thus estimated to be 2.40 cc./g. which is to be compared with 0.068 cc./g. for the second term. Therefore, a greater part of molecular weight dependence of ϕ_2 may be attributed to the end-group effect.

Finally, the authors will make a comparison between V_2 (see Table II) and the specific volume of solid PVA, V_2^0. The specific volume of completely amorphous PVA is estimated to be 0.787 from the extrapolation of the experimental values for PVA-film having different crystallinity[16]. A volume contraction in solution is clearly observed in the present case.

14) S. Orstein and F. Zernike, *Physik. Z.*, **27**, 261(1926).
15) The Chemical Society of Japan, "A Handbook of Chemistry (Kagaku Binran)", Maruzen Co., Ltd., Tokyo (1958), p. 461.

Summary

The solution density of polyvinyl alcohol dilute aqueous solution is measured by the use of the method of floating equilibria. This method is proved to be useful for the purpose of precise density and concentration determination of PVA dilute solution. An experimental formula for the density of PVA aqueous solution both as a function of the concentration and polymerization degree of PVA is proposed. The excluded volumes between solute and solvent are estimated from the molecular weight dependence of apparent and partial specific volumes obtained.

The authors wish to express their hearty thanks to Dr. Y. Kobatake of Tokyo Institute of Technology who calls their attention to the present problem; also to thank Professor M. Tamura of Kyoto University for his interest and guidance. They are also thankful to Dr. A. Nakajima of Kyoto University for his valuable suggestions in preparing the materials.

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16) I. Sakurada, Y. Nukushina and N. Mori, *Chemistry of High Polymers (Kobunshi Kagaku)*, **12**, 302 (1955).

Microwave Spectrum of Malononitrile, $CH_2(CN)_2$. I. The Molecular Structure in the Ground Vibrational State

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The vibration-rotation interaction in polyatomic molecules has been studied extensively by Nielsen and others[1]. The interaction manifests itself in several ways in the observed spectra; for example, the rotational constant differs slightly in each vibrational state and the centrifugal force results in the elongation of molecules. An interesting feature of the interaction is given by the Coriolis force which can be observed most clearly in the degenerate vibrational states. Microwave investigation has been made on the Coriolis interaction in linear and symmetric top molecules, in the name of *l*-type doubling[2]. However, it may be pointed out that, if the two vibrational states are nearly or accidentally degenerate, the Coriolis interaction is expected to become large. Malononitrile has been studied for this purpose, since the Coriolis interactions are expected between four low-lying C—C≡N bending modes[3].

The Raman effect of malononitrile was observed by Kohlrausch and Ypsilanti[4] and the infrared absorption spectrum was measured by Halverson and Francel[5]. The latter authors assigned the spectra and carried out the normal coordinate analysis. However, no data have yet been reported on the structure of the molecule. The present paper will give the molecular structure in the ground vibrational state. The vibration-rotation interaction will be treated in the near future.

Experimental

The apparatus used was a conventional Stark modulation spectrograph, a 100 kc. sine wave being used for simplicity[6]. In addition to the normal molecule, three kinds of molecules isotopically substituted, $CHD(CN)_2$, $CD_2(CN)_2$, and $CH_2CNC^{15}N$, were synthesized to observe their rotational spectra. The hydrogen atoms of malononitrile exchange readily with the hydrogen of water; thus, the deuterated molecules were obtained by mixing the normal malononitrile with heavy water, made slightly alkaline by adding a small quantity of anhydrous sodium carbonate. The ^{15}N substituted molecules were obtained as follows. Ammonium sulfate containing 23.5% ^{15}N was mixed with barium hydroxide and heated. The ammonia thus evolved was led into cold water. The reaction of aqueous ammonia with ethylcyanoacetate gave cyanoacetic amide, which was dehydrated by phosphorous oxychloride to $CH_2CNC^{15}N$[7].

Rotational Spectra and Rotational Constants

The malononitrile molecule has a twofold symmetry axis and the moment of inertia about this axis is of an intermediate magnitude. Thus, the selection rule allows only the *b*-type rotational transitions. The *a*-axis lies on a plane made by the two cyano groups and the central carbon atom. The *c*-type transitions are allowed for $CHD(CN)_2$ and the *a*-type transitions for $CH_2CNC^{15}N$, but neither of them was observed. Microwave absorption was observed only at room temperature since the vapor pressure is low. Owing to the large dipole moment (~3.6 D), the small rotational constants, and the presence of many vibrational states of low energies, the molecule was found to have many rotational lines: at least, one absorption line was observed in every 10 Mc./sec. Hence, the assignment seemed at first to be difficult. Fortunately, a *Q*-branch series $J_{0,J} \rightarrow J_{1\,J-1}$ was found to be assigned most easily*: the Stark effects are large and the intensities, in particular of high J members, are very strong. It was possible to resolve three or four Stark components of $J=5$, 6 and

1) H. H. Nielsen, *Revs. Modern Phys.*, **23**, 90 (1951).
2) See, for example, R. G. Shulman and C. H. Townes, *Phys. Rev.*, **77**, 421 (1950).
3) E. B. Wilson, Jr., *J. Chem. Phys.*, **4**, 313 (1936).
4) K. W. F. Kohlrausch and Gr. P. Ypsilanti, *Z. physik. Chem.*, **B29**, 274 (1935).
5) F. Halverson and R. J. Francel, *J. Chem. Phys.*, **17**, 694 (1949).
6) E. Hirota, T. Oka and Y. Morino, ibid., **29**, 444 (1958); This Bulletin, to be published.
7) H. Gilman, "Organic Syntheses", Vol. 1, John Wiley & Sons, Inc., New York (1948), p. 179; A. H. Blatt, ibid., Vol. 2 (1948), p. 379; A. R. Surrey, ibid., Vol. 25 (1945), p. 63.

* It can be easily shown by use of the rotational constants that the $J_{0J} \rightarrow J_{1,J-1}$ transitions are the single series of the *Q*-branch of this molecule in the region accessible by the present technique, 7000 to 30000 Mc./sec.

TABLE I. OBSERVED AND CALCULATED FREQUENCIES (Mc./sec.)

Transition	$CH_2(CN)_2$		$CH_2CNC^{15}N$		$CHD(CN)_2$		$CD_2(CN)_2$		$CH_2CN^{13}CN$
	obsd.	calcd.	obsd.	calcd.	obsd.	calcd.	obsd.	calcd.	obsd.
$1_{01} \rightarrow 1_{10}$	18265.36	18265.36	18088.67	18088.66	15916.73	15916.82	14077.66	14077.62	
$2_{02} \rightarrow 2_{11}$	18595.54	18595.46	18405.56	18405.88	16268.84	16268.81	14444.84	14444.81	
$3_{03} \rightarrow 3_{12}$	19098.79	19098.82	18889.37	18889.37	16807.95	16807.47	15008.56	15008.67	
$4_{04} \rightarrow 4_{13}$	19785.23	19785.23	19548.66	19548.23	17545.41	17545.45	15784.72	15784.65	
$5_{05} \rightarrow 5_{14}$	20667.93	20667.53	20394.99	20394.50	18498.82	18499.29	16791.92	16792.84	
$6_{06} \rightarrow 6_{15}$	21761.79	21761.37	21443.07	21442.81	19688.76	19688.98	18055.72	18057.16	
$7_{07} \rightarrow 7_{16}$	23084.25	23084.74	22709.58	22710.03	21135.78	21137.12	19601.55	19604.16	
$8_{08} \rightarrow 8_{17}$	24656.01	24657.52	24213.27	24214.85	22864.92	22867.70	21456.12	21461.10	
$9_{09} \rightarrow 9_{18}$	26497.38	26500.21	25973.43	25976.61	24899.76	24904.63	23645.34	23653.46	26367.03
$10_{0,10} \rightarrow 10_{19}$	28626.87	28632.98	28008.57	28014.56	27261.51	27269.52	26189.70	26202.06	28456.41
$0_{00} \rightarrow 1_{11}$	23498.82	23498.91	23189.52	23189.62	21086.78	21086.64	19191.00	19191.03	
$1_{01} \rightarrow 2_{12}$	28732.50	28732.46	28290.63	28290.58	26256.39	26256.46	24304.47	24304.45	
$5_{15} \rightarrow 6_{06}$	17414.02	17419.57							
$6_{16} \rightarrow 7_{07}$	23738.22	23746.58							
$5_{14} \rightarrow 4_{23}$	24093.24	24096.38							
$6_{15} \rightarrow 5_{24}$	17595.24	17586.45							

TABLE II. ROTATIONAL CONSTANTS AND PRINCIPAL MOMENTS OF INERTIA[a)]

	$CH_2(CN)_2$	$CH_2CNC^{15}N$	$CD_2(CN)_2$	$CHD(CN)_2$
A	20882.137	20639.146	16634.324	18501.730
B	2942.477	2863.585	2916.905	2931.189
C	2616.774	2550.477	2556.710	2584.910
b	-8.9961×10^{-3}	-8.7304×10^{-3}	-1.29590×10^{-2}	-1.09974×10^{-2}
I_a	24.208777	24.493794	30.390835	27.323445
I_b	171.8046	176.5378	173.3108	172.4662
I_c	193.1886	198.2104	197.7272	195.5701

$CH_2CN^{13}CN$

$A-(B+C)/2 = 18120.8\pm5.$ Mc./sec.

$(B-C)/2 = 160.3\pm4.$ Mc./sec.

a) Rotational constants are given in Mc./sec. and principal moments of inertia in amu Å^2. Conversion factor 505531 Mc. amu Å^2 is used.

7 lines and thus to check the J numbers of these lines by the technique of Golden and Wilson[8]. Six low J transitions of P- and R-branches were also observed for $CH_2(CN)_2$, and two R-branch transitions for isotopically substituted molecules. The Q-branch members, $9_{09} \rightarrow 9_{18}$ and $10_{0,10} \rightarrow 10_{19}$ of the $CH_2CN^{13}CN$ molecule in natural abundance were measured and assigned. The measured frequencies are listed in Table I.

The rotational constants given in Table II were determined by four Q-branch ($J=1$ to 4) and two R-branch ($0_{00} \rightarrow 1_{11}$ and $1_{01} \rightarrow 2_{12}$) transitions, the centrifugal distortion being neglected. $A-(B+C)/2$ and $(B-C)/2$ were obtained for $CH_2CN^{13}CN$. The results are also given in Table II. The frequencies calculated by using the constants obtained above are compared with the observed frequencies in Table I.

8) S. Golden and E. B. Wilson, Jr., *J. Chem. Phys.*, **16**, 669 (1948).

Structure Analysis

The structure of malononitrile is specified by five parameters: the C—H, the C—C, and the C≡N bond length, and the HCH and the CCC bond angle. If the linearity of the C—C≡N group is abandoned, an additional parameter, ∠CCN, is necessary.

For convenience a Cartesian coordinate system is fixed in the molecule; its origin coincides with the center of gravity and the x-axis is taken along to the c-axis, the y-axis to the a-axis, and the z-axis to the b-axis, respectively (see Fig. 1). For isotopically substituted molecules the origin is shifted to the new center of gravity,

TABLE III. THE x-, y- AND z-MOMENTS (amu Å^2)

	$CH_2(CN)_2$	$CH_2CNC^{15}N$	$CD_2(CN)_2$	$CHD(CN)_2$
$\sum m_i x_i^2$	1.4124	1.4106	2.9872	2.1805
$\sum m_i y_i^2$	170.3922	175.1228	170.3236	170.3564
$\sum m_i z_i^2$	22.7964	23.0876	27.4036	25.1430

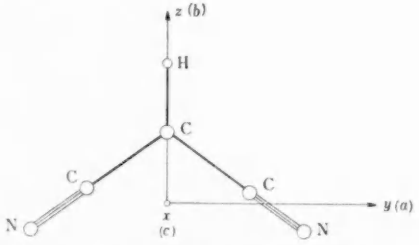

Fig. 1. Schematic diagram of malononitrile molecule.

but the x-, y-, and z-axes are kept parallel to those in the original molecule. For $CD_2(CN)_2$ the (x, y, z) system evidently coincides with the principal axes of moment of inertia, but for $CHD(CN)_2$ and $CH_2CNC^{15}N$ a slight rotation of axes is necessary, in transforming from the (a, b, c) system to the (x, y, z) system. Thus, in evaluating $\sum m_i x_i^2$, $\sum m_i y_i^2$, and $\sum m_i z_i^2$ (which are called the x-moment, the y-moment, and the z-moment, respectively) from I_a, I_b and I_c for the latter two molecules, some minor corrections are necessary and they are easily calculated by assuming a structure close to the real one. The x-, y- and z-moments thus obtained are listed in Table III.

a) x-Coordinates. — The x-moment is a function only of the x-coordinate of the hydrogen atom, x_H: that is,

$$\sum m_i x_i^2 = 2m x_H^2 \qquad (1)$$

where $2m = 2m_H$ for $CH_2(CN)_2$ and $CH_2CN \cdot C^{15}N$, $2m = [(3m_C + 2m_N)(m_D + m_H) + 4m_D m_H]/(3m_C + 2m_N + m_D + m_H)$ for $CHD(CN)_2$, and $2m = 2m_D$ for $CD_2(CN)_2$. The value of x_H, given in Table IV, increases with the mass of hydrogen, just as in the case of methylene chloride. Laurie[9] has explained this effect by the inertia defect, in analogy with planar molecules. By taking into consideration the inertia defect Δ, Eq. 1 is modified as follows:

$$\sum m_i x_i^2 + (1/2)\Delta = 2m x_H^2 \qquad (1')$$

where a single value of the inertia defect Δ is assumed for all molecules, since the inertia defect is considered to originate from the in-plane vibrations of low frequencies. In fact, four observed x-moments can be reproduced by Eq. 1', if two parameters, x_H and Δ, are assumed to be 0.8847 Å and 0.3379 amu Å^2, respectively. The calculated x-moments are compared with those observed in Table V. The inertia defect Δ of 0.3379 amu Å^2 is large compared with that of methylene chloride 0.167 amu Å^2, or of other molecules[9]. It is consistent with the fact that there are more normal modes of low frequencies in malononitrile.

TABLE IV. VALUES OF x_H DETERMINED WITHOUT THE INERTIA DEFECT CORRECTION (Å)

Molecule	x_H
$CH_2(CN)_2$	0.8370
$CH_2CNC^{15}N$	0.8364
$CHD(CN)_2$	0.8514
$CD_2(CN)_2$	0.8610

TABLE V. OBSERVED AND CALCULATED x-MOMENTS (amu Å^2)

Molecule	$\sum m_i x_i^2$	
	obsd.	calcd.[a]
$CH_2(CN)_2$	1.4124	1.4091
$CH_2CNC^{15}N$	1.4106	1.4091
$CHD(CN)_2$	2.1805	2.1851
$CD_2(CN)_2$	2.9872	2.9848

a) $x_H = 0.8847$ Å and $\Delta = 0.3379$ amu Å^2 are assumed.

Myers and Gwinn[10] have analyzed their data on methylene chloride by plotting x_H against $1/2m$. The meaning of this procedure is evident from Eq. 1'; if $\Delta \ll \sum m_i x_i^2$ is assumed, x_H is given by $(\sum m_i x_i^2/2m)^{1/2} \cdot (1 + \Delta/4\sum m_i x_i^2) = x_H^0 + (\Delta/4x_H^0)(1/2m)$, where $x_H^0 = (\sum m_i x_i^2/2m)^{1/2}$ means the value of x_H, when Δ is ignored. Thus, the x_H obtained here corresponds to x_H^0 in the limit of $1/2m \to 0$.

b) y-Coordinates. — If the effect of zero-point vibration is negligible, the same y-moment should be obtained for three molecules; $CH_2(CN)_2$, $CHD(CN)_2$ and $CD_2(CN)_2$, since the y-moment is a function depending only upon the coordinates of the cyano groups. The observed y-moments,

9) V. W. Laurie, ibid., **28**, 704 (1958).

10) R. J. Myers and W. D. Gwinn, ibid., **20**, 1420 (1952).

170.3922, 170.3564 and 170.3236 amu Å^2, show a small discrepancy, presumably due to zero-point vibration, but the effect is not so large as in the x-moment.

By combining the y-moment for $CH_2CN\cdot C^{15}N$, $(\sum m_i y_i^2)_{15}$, with that of $CH_2(CN)_2$, $(\sum m_i y_i^2)_{14}$, the y-coordinate of nitrogen, y_N, in the normal molecule is obtained as follows:

$$y_N^2 = [(M+\Delta m_N)/M\Delta m_N] \times [(\sum m_i y_i^2)_{15} - (\sum m_i y_i^2)_{14}] \quad (2)$$

where M is the total mass of $CH_2(CN)_2$, and Δm_N is the mass difference of ^{15}N and ^{14}N. Then y_N is found to be 2.1943 Å.

In order to determine the y-coordinate of the carbon atom in a cyano group, y_C, it is desirable to substitute the carbon atom with its isotope, ^{13}C[11]. As mentioned earlier, two Q-branch transitions have been observed for $CH_2CN^{13}CN$ molecule, but the rotational constants could not be determined accurately enough for the structure analysis. Hence y_C is evaluated through the y-moment combined with the value of y_N obtained above. Three values of the y-moments for $CH_2(CN)_2$, $CHD(CN)_2$, and $CD_2(CN)_2$ give accordingly three y_C's: 1.2161, 1.2155 and 1.2149 Å, respectively. As the difference between them is not large, the average of the three values is used for y_C: that is, 1.2155 Å.

c) z-Coordinates. — The z-moments of $CH_2(CN)_2$, $(\sum m_i z_i^2)_2$, and of $CHD(CN)_2$, $(\sum m_i z_i^2)_3$, give the z-coordinate of hydrogen in the normal molecule, z_H, by the relation similar to Eq. 2:

$$z_H^2 = [(M+\Delta m_H)/M\Delta m_H] \times [(\sum m_i z_i^2)_3 - (\sum m_i z_i^2)_2] \quad (3)$$

where Δm_H is the mass difference of D and H. If the z-moment of $CD_2(CN)_2$, $(\sum m_i z_i^2)_4$, is used in place of $(\sum m_i z_i^2)_3$, the equation

$$z_H^2 = [(M+2\Delta m_H)/2M\Delta m_H] \times [(\sum m_i z_i^2)_4 - (\sum m_i z_i^2)_2] \quad (4)$$

must be applied. Eq. 3 gives z_H of 1.5384 Å, whereas Eq. 4 gives 1.5357 Å. The average value, 1.5371 Å, is used in the following analysis of the structure.

A similar procedure is used to determine the z-coordinate of the nitrogen atom, z_N. The relevant equation is

$$z_N^2 = [(M+\Delta m_N)/M\Delta m_N] \times [(\sum m_i z_i^2)_{15} - (\sum m_i z_i^2)_{14}] \quad (5)$$

where $(\sum m_i z_i^2)_{14}$ means $(\sum m_i z_i^2)_2$ in Eqs. 3 and 4. It may be noted that, since the effect of zero-point vibration entering in $\sum m_i x_i^2$ is probably similar for the two molecules $CH_2(CN)_2$ and $CH_2CNC^{15}N$, I_{yy} is used in place of $(\sum m_i z_i^2)$. In doing so, the accuracy attained becomes considerably better, for the value of I_{yy} is determined by the rotational constant A, whereas $\sum m_i z_i^2$ is evaluated by three rotational constants, A, B and C. Under this assumption z_N is found to be -0.5427_3 Å.

Since adequate substitutions are not yet available, a procedure similar to that used for the determination of z_H and z_N can not be applied to the z-coordinates of carbon atoms. Moreover, whatever substitution is possible, the z-coordinate of the carbon atom of the cyano group is close to zero, and the procedure becomes less powerful. Hence the first moment equation and the relation giving the z-moment of $CH_2(CN)_2$ are used to evaluate the z-coordinates of the apex carbon atom, z_0, and of the carbon atom in the cyano group, z_C[11]. They are 0.8994 and 0.0545 Å, respectively.

All the coodinates necessary for the structure determination are thus obtained and listed in Table VI. The bond length

Table VI. Coordinates of atoms in $CH_2(CN)_2$ and molecular structure

Atom	x_i	y_i	z_i
H	± 0.8847 Å	0 Å	$+1.5371$ Å
C (apex)	0	0	$+0.8994$
C (cyano)	0	± 1.2155	$+0.0545$
N	0	± 2.1943	-0.5427_3

C—C	$1.480_3 \pm 0.0056$ Å	∠CCC	110°24′±24′
C≡N	$1.146_6 \pm 0.0064$ Å	∠HCH	108°26′±26′
C—H	$1.090_6 \pm 0.0034$ Å	∠CCN	180°−(3°24′±26′) (outside)

of C—H is found to be 1.091 Å, that of C—C 1.480 Å, and that of C≡N 1.147 Å. The bond angle of CCC, 110°24′, is about 1° wider than the tetrahedral angle, whereas that of HCH, 108°26′, is smaller than the tetrahedral angle by the same order of magnitude. Myers and Gwinn[10] reported the C—H bond length and the HCH bond angle in methylene chloride to be 1.082 Å and 112°58′, respectively, whereas Lide, Jr.[12], obtained 1.092 Å and 111°52′, for the corresponding quantities in methylene fluoride. The C—H bond length of malononitrile, 1.091 Å, is closer to that of methylene fluoride, rather than to that of methylene chloride, but the

11) C. C. Costain, ibid., **29**, 864 (1958).

12) D. R. Lide, Jr., *J. Am. Chem. Soc.*, **74**, 3548 (1952).

HCH bond angle 108°26′ is definitely smaller than those of methylene halides. It is noteworthy that the linearity of C—C≡N groups does not hold, the cyano groups being bent outside by about 3.5°. Though zero-point vibration may modify considerably the equilibrium configuration, it seems reasonable to assume an electrostatic repulsion between two electronegative groups such as cyano radicals. Somewhat longer C—C, somewhat shorter C≡N bond length, and the bent C—C≡N indicate that the electron configuration in the cyano groups might be more or less different from that in acetonitrile. In fact, Casabella and Bray[13] found, in the solid state, a quadrupole coupling constant and an asymmetry parameter, definitely larger than those of acetonitrile and of ethyl cyanide.

Dipole Moment

The dipole moment of $CH_2(CN)_2$ was obtained from the Stark effects of the six transitions: four Q-branch lines of $J=1$ to 4 and two R-branch transitions, $0_{00}\rightarrow 1_{11}$ and $1_{01}\rightarrow 2_{12}$. The field strength was calibrated by the $J=1\rightarrow 2$ transition of OCS, the dipole moment of OCS being assumed to be 0.7124 D[14]. The values of the dipole moment obtained from the six transitions agree well with each other (Table VII), The average of them is 3.735 D, which is compared with 3.6 D obtained by the dielectric constant measurement in benzene solutions[15].

13) P. A. Casabella and P. J. Bray, *J. Chem. Phys.*, **29**, 1105 (1958).
14) S. A. Marshall and I. Weber, *Phys. Rev.*, **105**, 1502 (1957).

TABLE VII. DIPOLE MOMENT (DEBYE)

Transition	μ
$1_{01}\rightarrow 1_{10}$	3.724
$2_{02}\rightarrow 2_{11}$	3.735
$3_{03}\rightarrow 3_{12}$	3.759
$4_{04}\rightarrow 4_{13}$	3.750
$0_{00}\rightarrow 1_{11}$	3.704
$1_{01}\rightarrow 2_{12}$	3.736
average	3.735 ± 0.017

The authors wish to express their sincere thanks to Dr. Makoto Shima, Institute for Physical and Chemical Research, for supplying them heavy water and ammonium sulfate containing 23.5% ^{15}N. The expenses of this research were defrayed from the Scientific Research Encouragement Grant of the Ministry of Education to which the authors' thanks are also due.

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Added in Proof:

October, 1959 Dr. P. W. Moore of Purdue University called the authors' attention to the paper by N. Muller and D. E. Pritchard, *J. Am. Chem. Soc.*, **80**, 3483 (1958). They measured the microwave spectrum of normal species $CH_2(CN)_2$ of malononitrile and obtained rotational constants in close agreement with the authors'. Recently Dr. Muller wrote us that their measurement had been extended to include the rotational spectrum of deuterium substituted species $CD_2(CN)_2$, and the rotational constants obtained were also in agreement with the authors'.

15) P. Trunel, *Ann. chim.*, **12**, 93 (1939).

The Adsorption of Dye Mixtures by Cellophane Sheet. I. Temperature and Concentration Dependence of Adsorption from Some Binary Mixtures

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It is well known that the amount of adsorption of dyes from binary mixtures of a direct dye with others is commonly reduced as compared with the adsorbed dye amount when dyed singly[1-3]. Some factors of such reduction of adsorption in mixture dyeing have been variously discussed, and it seems to be most appropriate to consider a mutual interaction between dyes in solution as a principal factor. Neale and Stringfellow have considered that such interaction is attributed to the complex formation[2]. This concept, however, has failed to be accepted, because there is no direct evidence of complex formation in solution at such a high temperature as is practically applied[4]. Derbyshire and Peters[3] have recently shown by the spectroscopic measurements that Chlorazol Sky Blue FF and Chrysophenine G form a 1 : 1 complex in aqueous solution containing no salt at 60°C, and further concluded by the thermodynamic treatment that the complex formation occurs even at a usual dyeing temperature 90°C. Based on this conclusion, they have discussed in a semi-quantitative way the results of mixture dyeing.

In the hope of finding a method to obtain some quantitative information about the interaction between dyes in mixture dyebath, necessary to explain the reduction in adsorption, the authors have studied the single and the mixture dyeings of Chlorazol Sky Blue FF and Chrysophenine G, and of Chlorazol Sky Blue FF and a monoazo acid dye.

Experimental

Chlorazol Sky Blue FF and Chrysophenine G were used as direct dyes, and *p*-nitroaniline→γ acid (α-coupling) as a monoazo acid dye. Chlorazol Sky Blue FF (called Blue dye for short) and the monoazo acid dye (Acid dye) were the same as those used in the authors' previous works[5,6], and Chrysophenine G (Yellow dye) was prepared by purifing the commercial dye by Robinson and Mills' method[7].

The Cellophane sheet used was that made by Tokyo Cellophane Co., Ltd. It was washed with distilled water at 90°C for 30 min. Pieces of the sheet weighing 15~25 mg. were dyed in 75 g. portions of the dye solution at 50, 70 and 90°C for 24 hr.* The dyed sheets were rinsed in ice-cold water (about 6°C) and then left in a desiccator with 50% sulfuric acid for two days. An accurate weight of the dyed sheet was obtained by dividing its weight under the constant humidity by a known humidity coefficent (e. g. 1.07 at 15°C and 1.10 at 30°C)[8].

Check measurements on solutions of known density in 25% aqueous pyridine showed that the dyes obeyed Beer's law both singly and in mixture, and that the absorption spectra in the mixture were additive. Based on this fact, the dye adsorbed by the sheet was stripped with 25% aqueous pyridine and the dye content of the strip solution was measured by a Shimadzu QR-50 spectrophotometer.

In case of the mixture dyeing, the initial concentration of Blue dye was about 1×10^{-5} mol./l. for every dyebath, and those of Yellow dye and Acid dye were varied from zero to about 35×10^{-5} and 90×10^{-5} mol./l., respectively. The concentration of sodium chloride was 2.0 g./l. for every dyebath.

Results

The relation between the amount of adsorption of Blue dye and the dyebath concentration of its partners was examined, 24 hr. after mixture dyeing, by the

1) J. Boulton, A. E. Delth, F. Forthergrill and T. H. Morton, *J. Textile Inst.*, **24**, 113 (1933).
2) S. M. Neale and W. A. Stringfellow, *J. Soc. Dyers Colourists*, **59**, 241 (1943).
3) A. N. Derbyshire and R. H. Peters, ibid., **72**, 268 (1956).
4) T. Vickerstaff, "The Physical Chemistry of Dyeing", 2nd Ed., Oliver & Boyd, London (1954), p. 242.
5) Y. Tanizaki, T. Kobayashi and N. Ando, This Bulletin, **32**, 119 (1954).
6) T. Kobayashi, Y. Tanizaki and N. Ando, ibid., **32**, 675 (1959).
7) C. Robinson and H. A. T. Mills, *Proc. Roy. Soc. (London)*, **A131**, 576 (1931).
8) K. Nishida, *J. Soc. Textile Cellulose Ind. Japan (Sen-i Gakkaishi)*, **7**, 539 (1951).

* This time of of dyeing (24 hr.) may be enough for only a qualitative discussion of the behavior of mixture dyeing.

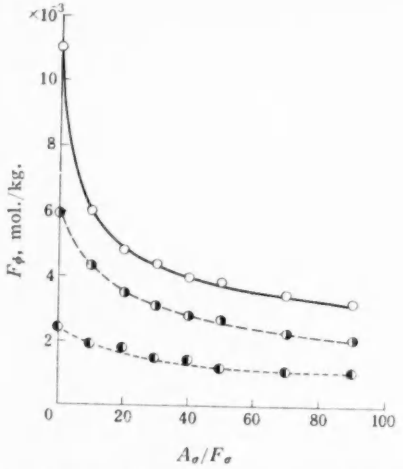

Fig. 1. The relation between the adsorption of Blue dye (F_ϕ) from a mixture dyebath with Acid dye and the ratio of final dyebath concentration of Acid dye (A_σ) to that of Blue dye (F_σ).
—○— 50°C, --◑-- 70°C, ---◐--- 90°C

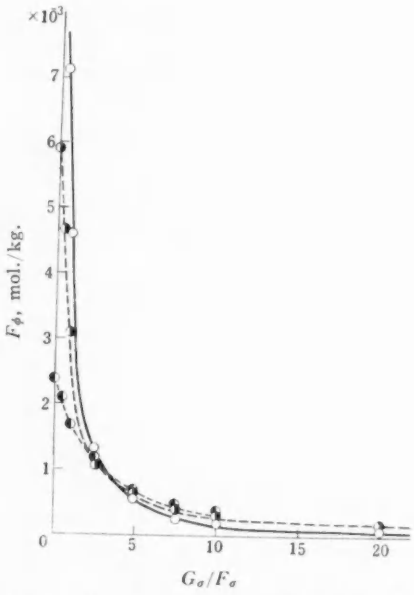

Fig. 2. The relation between the adsorption of Blue dye (F_ϕ) from mixture dyebath with Yellow dye and the ratio of final dyebath concentration of Yellow dye (G_σ) to that of Blue dye (F_σ).
—○— 50°C, --◑-- 70°C, ---◐--- 90°C

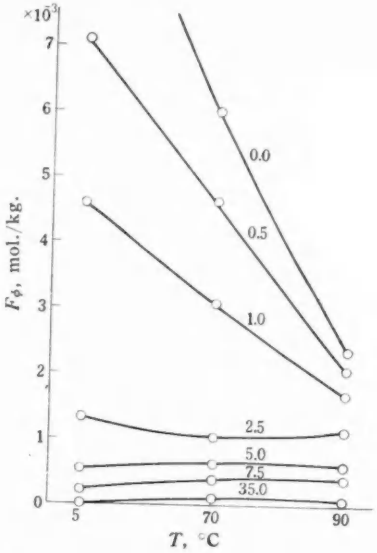

Fig. 3. Effect of temperature on the adsorption of Blue dye from mixture dyebath. The numbers indicate the ratio of the initial dyebath concentration of Yellow dye to that of Blue dye.

adsorption measurements of binary mixtures containing a constant amount of Blue dye. The results are shown in Figs. 1 and 2; the one denotes the pair of Blue dye and Acid dye, and the other Blue dye and Yellow dye. Comparison between these figures shows that the adsorption of Blue dye is not so decreased with an increase in the dyebath concentration of Acid dye (Fig. 1), while it is markedly reduced by the addition of a very small amount of Yellow dye until it rapidly converges to zero (Fig. 2). Furthermore, under the present condition, the adsorption of Blue dye from a dyebath, containing several times as much Yellow dye as Blue dye, slightly increases with a raise in temperature; this is the same tendency as that reported by Neale and Stringfellow[2]. This situation can be recognized by the relation between the adsorption of Blue dye and temperature in Fig. 3.

In case of mixture dyeing with Blue dye the adsorption of the partner, i. e. Yellow dye or Acid dye, is also reduced, as compared with that in the case of its single dyeing. For instance, adsorption curves of Yellow dye from single and mixture dyebaths at 70°C, corresponding to Fig. 2, are shown in Fig. 4a.

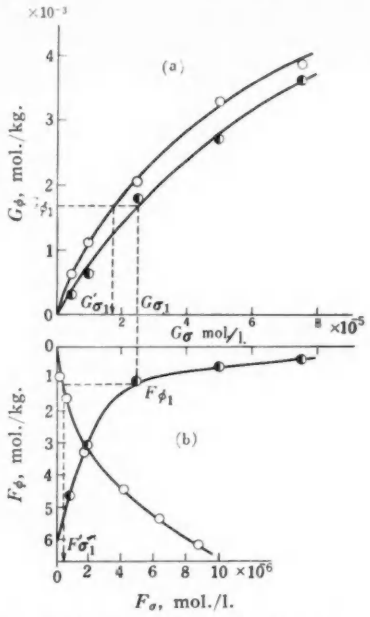

Fig. 4. The adsorptions of Blue dye and Yellow dye from single and mixture dyebaths at 70°C. Here the results of mixture dyeing co respond to those of Fig. 2. Scale (F_σ) on the abscissa (b) refers to the white circles.

○ Single ◐ Mixture

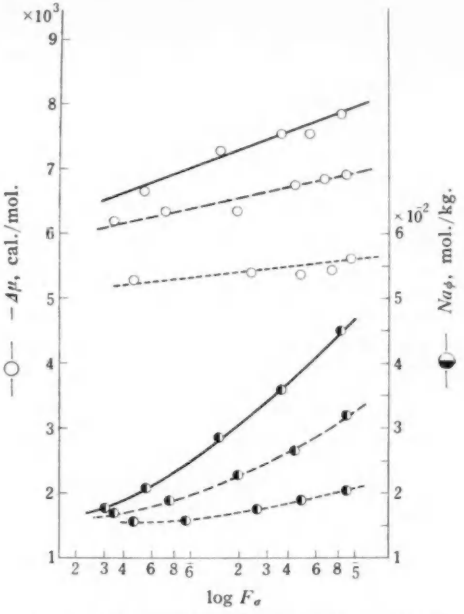

Fig. 5. The relations of the affinity ($-\Delta\mu^0$) of Blue dye for Cellophane (white circles) and of the concentration of sodium ion (Na_ϕ) in Cellophane (half solid circles) to the logarithm of final dyebath concentration of Blue dye (F_σ, mol./l.).

—— 50°C, ---- 70°C, ------ 90°C

It has been seen that the affinity of Blue dye**, obtained from its single dyeing (corresponding to the white circles in Fig. 4b), is more or less dependent on its dyebath concentration at constant temperature. The relation between the affinity of Blue dye and its final dye bath concentration at various temperatures in single dyeing is shown in Fig. 5. This figure shows that the affinity, $-\Delta\mu^0$, is approximately proportional to the logarithm of the final dyebath concentration of Blue dye, F_σ. In this figure is also shown the relation between log F_σ and the concentration of sodium ion in Cellophane, Na_ϕ**.

Discussion

Based on the assumption that the reduction of the amount of dyes resulting from the mixture dyeing is due to an interaction between the two dyes, the results described in the preceding section will be discussed. Now, let us assume simply that:

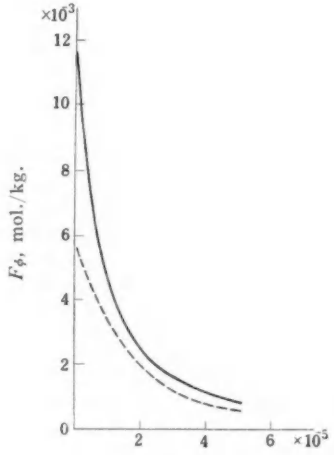

Fig. 6. The relation between the dyebath concentration of Yellow dye and the adsorption of Blue dye calculated from Eqs. 1 and 3. $F_\sigma = 1\times10^{-5}$ mol./l., $K_{50°} = 6\times10^{-7}$ mol./l., $K_{70°} = 1\times10^{-6}$ mol./l.

—— 50°C, ---- 70°C

** Na_ϕ and $-\Delta\mu^0$ were calculated from Eqs. 7.19 (p. 200) and 7.26 (p. 206) in Ref. 4. V (surface layer volume) =0.45 l./kg. for each dyeing temperature.

1) The effective dyebath concentration which contributes to adsorption is reduced by an interaction between both dyes in mixture.

2) The amount of the dye adsorbed from the mixture dyebath corresponds to this effective dyebath concentration, and the adsorbing behavior of the dye in mixture dyeing is just the same as that in its single dyeing, so it behaves independently. Consequently, concerning the effective dyebath concentration, the additivity in adsorption comes into being.

These assumptions may be appropriate under the condition that no competition of dyes for the available surface occurs. If the assumptions are accepted, the effective dye bath concentration will be calculated by the following equation, using the amount of dye adsorbed from mixture dyeing and its affinity obtained from single dyeing,

$$D_\phi = Na_\phi^{-z} Na_\sigma^{+z} V^{z+1} D_\sigma' \exp(-\Delta\mu^0/\boldsymbol{R}T) \tag{1}$$

where D_ϕ (mol./kg.) is the amount of a dye adsorbed by Cellophane, D_σ' (mol./l.) the effective dyebath concentration, Na_ϕ (mol./kg.) the sodium ion concentration in Cellophane, Na_σ (mol./l.) the sodium ion concentration in dyebath, V (l./kg.) the surface layer volume, $-\Delta\mu^0$ (cal./mol.) the standard affinity, $\boldsymbol{R}$ and T the gas constant and the absolute temperature, respectively, and z the number of sulfonic groups per molecule. The difference D_c (mol./l.) between the total dyebath concentration D_σ (mol./l.) and the effective dyebath concentration may be attributed to the interaction of dyes in mixture solution; in other words, D_c may be regarded as the dyebath concentration ineffective to adsorption. If the amount of a dye adsorbed in this mixture dyeing is known, it would be expected that its effective dyebath concentration would be calculated by Eq. 1. However, as the calculated affinity of dyes generally varies more or less with the dyebath concentration, it is undesirable to calculate it directly by Eq. 1. Therefore, it was obtained graphically from the observed values in single and mixture dyeings. Concerning the pair of Blue dye and Yellow dye, for example, its effective dyebath concentration is obtained from Figs. 4a and 4b as follows: when the final total dye bath concentrations of Blue dye and Yellow dye are $F_{\sigma 1}$ and $G_{\sigma 1}$, respectively***, as shown in the figure, the amounts of adsorption of the dyes $F_{\phi 1}$, $G_{\phi 1}$ correspond to $F_{\sigma 1}'$, $G_{\sigma 1}'$ in single dyeing, respectively, which may be regarded as their effective dyebath concentrations. $F_{\sigma 1}-F_{\sigma 1}' \equiv F_{c1}$ and $G_{\sigma 1}-G_{\sigma 1}' \equiv G_{c1}$ may be regarded as the concentrations participated in the interaction, and it follows that G_{c1}/F_{c1} means the mole ratio of both dyes contributed to the interaction. Values obtained in such a way are shown in Tables I and II. Table I shows that G_c/F_c tends to about unity when the relative concentration of Yellow dye to Blue dye increases to a certain value. If it is assumed that the interaction in this range of concentration means the formation of a 1:1 complex, it is possible to calculate the instability constant K of the complex, according to the mass action law,

$$K = \frac{F_\sigma' G_\sigma'}{F_c} = \frac{(F_\sigma - F_c)(G_\sigma - G_c)}{F_c}, \quad (F_c = G_c) \tag{2}$$

Values of K calculated by the equation are shown in Table I.

When the value of K is known, the effective dyebath concentration will be obtained from Eq. 2. For example, F_σ' can be given as a function of F_σ and G_σ, by the following equation which was derived from Eq. 2,

$$F_\sigma' = F_\sigma - F_c = \frac{1}{2}\{(G_\sigma - a)^2 + (b^2 - a^2)\}^{1/2} + \frac{1}{2}(a - G_\sigma) \tag{3}$$

where $a = F_\sigma - K$ and $b = F_\sigma + K$. Since a and b are constant when F_σ is fixed, F_σ' is the function of G_σ alone. Further, the value of F_ϕ in the mixture of Blue dye and Yellow dye can be obtained by substituting F_σ' into Eq. 1.

In order to check the validity of the assumption described above, values of F_σ' corresponding to various values of G_σ were calculated by Eq. 3; here were used 6×10^{-7} and 1×10^{-6} mol./l. as the values of $K_{50°}$ and $K_{70°}$, respectively, and 1×10^{-5} mol./l. as that of F_σ and $0.5\times10^{-5}\sim5\times10^{-5}$ mol./l. as that of G_σ. The values of F_ϕ are also calculated by Eq. 1, using the obtained values of F_σ', where Na_ϕ and $-\Delta\mu^0$ were obtained graphically from Fig. 5, and 3.42×10^{-2} mol./l. and 0.45 l./kg. were used as the values of Na_σ and V, respectively. These calculated values of F_ϕ against

*** Since the total concentration of Blue dye is nearly constant (1×10^{-5} mol./l.), $G_{\sigma 1}/F_{\sigma 1}$ is dependent only on $G_{\sigma 1}$. Suffix 1 denotes some fixed values of F_σ, G_σ, etc.

TABLE I. RESULTS OF MIXTURE DYEING OF BLUE DYE AND YELLOW DYE

T°C	F_σ $\times10^6$ mol./l.	F_ϕ $\times10^3$ mol./kg.	F_σ' $\times10^6$ mol./l.	F_c $\times10^6$ mol./l.	G_c/F_c	K, mol./l.	G_c $\times10^6$ mol./l.	G_σ' $\times10^6$ mol./l.	G_ϕ $\times10^3$ mol./kg.	G_σ $\times10^6$ mol./l.
50	8.04	7.1	3.2	4.8	0.7	—	3.3	1.5	0.6	4.83
	8.88	4.6	1.3	7.6	0.7	—	5.1	4.6	1.3	9.70
	9.75	1.3	0.4	9.4	1.2	4.7×10^{-7}	11.0	14.0	2.8	24.5
	9.87	0.6	0.2	9.7	1.2	7.4×10^{-7}	12.0	37.0	5.2	48.8
70	8.59	4.6	4.6	4.0	0.7	—	2.6	2.3	0.3	4.89
	9.39	3.1	2.1	7.3	0.5	—	3.6	6.3	0.6	9.87
	9.73	1.1	0.4	9.3	0.5	—	4.6	20.0	1.8	24.6
	9.86	0.6	0.3	9.6	1.3	9.6×10^{-7}	12.0	37.0	2.7	49.4
90	9.90	0.4	0.9	9.0	0.9	7.4×10^{-6}	8.0	70.0	1.7	78.0
	9.96	0.2	0.7	9.3	1.0	1.4×10^{-5}	9.0	190.0	3.5	199.0

Notations, F_σ etc. and G_σ etc., refer to Blue dye and Yellow dye, respectively.
K means the instability constant of complex. $(F_c+G_c)/2$ was regarded as the concentration of complex in the range $0.9\leq G_c/F_c\leq1.3$.

TABLE II. RESULTS OF MIXTURE DYEING OF BLUE DYE AND ACID DYE

T°C	F_σ $\times10^6$ mol./l.	F_ϕ $\times10^3$ mol./kg.	F_σ' $\times10^6$ mol./l.	F_c $\times10^6$ mol./l.	A_c/F_c	A_c $\times10^6$ mol./l.	A_σ' $\times10^5$ mol./l.	A_ϕ $\times10^3$ mol./kg.	A_σ $\times10^4$ mol./l.
50	8.98	4.9	1.4	7.6	1.1	8	1.2	1.6	2.0
	8.96	4.4	1.2	7.8	1.2	9	2.1	2.2	3.0
	9.14	4.0	1.0	8.1	1.4	11	2.9	2.6	4.0
	9.15	3.5	0.9	8.3	1.4	28	4.2	3.2	7.0
70	9.25	3.1	2.0	7.3	2.3	17	1.3	1.5	3.0
	9.36	2.8	1.7	7.7	2.7	21	1.9	1.8	4.0
	9.47	2.3	1.2	8.3	3.3	27	4.3	2.6	7.0
	9.55	2.1	1.1	8.5	3.4	29	6.1	3.1	9.0
90	9.61	1.8	5.4	4.2	1.9	8	1.2	0.8	2.0
	9.67	1.4	3.7	6.0	2.4	14	2.6	1.3	4.0
	9.73	1.3	3.1	6.6	3.0	20	3.0	1.5	5.0
	9.73	1.1	2.5	7.2	3.3	24	4.6	1.9	7.0
	9.76	1.1	2.5	7.3	3.5	25	6.5	2.3	9.0

Notations, F_σ etc. and A_σ etc., refer to Blue dye and Acid dye, respectively.

G_σ are given in Fig. 6. Good agreement between the calculated (Fig. 6) and the measured (Fig. 2) values shows that the behavior of dyes in mixture dyeing may be qualitatively explained by the knowledge of single dyeing, if it is possible to know the instability constant.

If the composition of complexes remains constant over the whole concentration range, K should be determined in principle even when the composition is not 1:1. In this way the amount of dyes adsorbed from mixture dyeing may be predicted. In the case of the mixture of Blue dye and Acid dye, however, the composition is gradually varied****, so the instability constant could not be obtained. Therefore, the amount of adsorption of the dyes from mixture dyeing can not be calculated by the above method. But it is expected that the difference between Fig. 1 and Fig. 2 may be understood qualitatively as follows: it is dependent directly on the extent of decrease in the effective dyebath concentration of Blue dye whether the reduction in adsorption of this dye is slow (Fig. 1) or rapid (Fig. 2) with an increase in the dyebath concentration of its partners. This fact may be attributed to the following two factors:

(a) The mole ratio of components in complexes.

(b) The instability constant of the complexes.

It is clear that the smaller the mole ratio (G_c/F_c or A_c/F_c), the greater the

**** The spectroscopic measurements for the same mixture free from sodium chloride at room temperature show the same tendency: A_c/F_c gradually increases with an increase in the relative concentration of Acid dye.

TABLE III. EFFECT OF TEMPERATURE ON THE ADSORPTION OF BLUE DYE

G_o/F_o	T°C	$\Delta \ln F_o'/\Delta T$	$-4\Delta \ln Na_\phi/\Delta T$	$\Delta(-\Delta\mu^0/RT)/\Delta T$	$\Delta \ln F_\phi/\Delta T$
0.5	50	−0.0005	+0.0677	−0.100	−0.037
	70	+0.0154	+0.0708	−0.165	−0.079
	90				
5.0	50	+0.0137	+0.0118	−0.060	−0.034
	70	+0.1035	+0.0062	−0.120	−0.014
	90				
10.0	50	+0.0142	+0.0121	−0.045	−0.019
	70	+0.1097	+0.0129	−0.115	+0.008
	90				

decrease in effective dyebath concentration of Blue dye. If one considers only this point, it will apparently be expected from Tables I and II that the reduction of F_ϕ is slower in the case of the pair of Acid dye and Blue dye than that of Yellow dye and Blue dye. On the other hand, when the complexes have the same composition, the smaller K is, the greater should be the decrease in the effective dye bath concentration. For instance, it will be expected that in the case of the pair of Acid dye and Blue dye the value of K at a given temperature is greater than in the case of that of Yellow dye and Blue dye in a concentration range, in which only a 1 : 1 complex seems to be formed in both pairs[9]. Concerning the effect of temperature, the reduction in adsorption of a dye on addition of its partner will become smaller with temperature, since the value of K increases in general with the rise of temperature. This is clearly seen in Figs. 1 and 2.

The relation between the amount of Blue dye adsorbed from the mixture with Yellow dye and dyeing temperature, as shown in Fig. 3, is also remarkable. That is, the amount of Blue dye adsorbed from the mixture, which contains several times as much Yellow dye as Blue dye, tends to increase slightly with the rise of temperature. The interpretation of this result is rendered difficult, but it may be explained at least by the hypothesis of complex formation and the knowledge of single dyeing. In other words, if Na_ϕ and V are independent of temperature, the partial differentiation of Eq. 1 with respect to T leads to

$$\frac{\partial \ln F_\phi}{\partial T} = -4\frac{\partial \ln Na_\phi}{\partial T} + \frac{\partial \ln F_o'}{\partial T} + \frac{\partial}{\partial T}\left(\frac{-\Delta\mu^0}{RT}\right) \tag{4}$$

To see the correspondence of the equation with the results in Fig. 3, the value of each term at the right side of Eq. 4 was calculated for the interval of 20°C (50~70 and 70~90°C). If one takes 1×10^{-5} mol./l. as F_o, 1 : 0.5, 1 : 5 and 1 : 10 as F_o/G_o, and 5×10^{-7}, 1×10^{-6} and 5×10^{-5} mol./l. as K of the 1 : 1 complex at 50, 70 and 90°C, respectively, then F_o' at each temperature can be calculated from Eq. 3, and Na_ϕ and $-\Delta\mu^0$ can be obtained from Fig. 5, also. Therefore, the value of $\Delta \ln F_\phi/\Delta T$ can be obtained from Eq. 4. They are listed in Table III. The result agrees qualitatively with the relation between F_ϕ and the temperature shown in Fig. 3. It will be recognized here that the sign of $\partial \ln F_\phi/\partial T$ may be dependent chiefly on the relation between the second and the third terms. In other words, it may mostly be influenced by the dependence of the instability constant and the affinity on temperature.

9) A value of K of the mixture in aqueous solution of Blue dye and Acid dye calculated at room temperture for a concentration range, in which only a 1 : 1 complex seems to be formed, is 1.25×10^{-5} (Ref. 6) and that of the mixture of Blue dye and Yellow dye is 4×10^{-6} at 60°C (Ref. 3). If these values are compared with each other at the same temperature, the difference between them will become greater: K of the former may be much greater than that of the latter.

Summary

1) The amount of dyes adsorbed by Cellophane from two mixture dyeings of Chlorazol Sky Blue FF and Chrysophenine G, and Chlorazol Sky Blue FF and *p*-nitroaniline→γ acid (α-coupling) was measured. Further, the amount in case of single dyeing was also measured.

2) It was assumed that the reduction in adsorption of dyes from mixture dyeing is due to an interaction between the two dyes in the dyebath, and that this interaction means only the formation of complexes. On this assumption, the instability constant in the case of the pair of Blue dye

and Yellow dye was calculated, according to the mass action law, but it was impossible to calculate it in the case of the pair of Acid dye and Blue dye, because the composition of complexes of this pair was not constant.

3) How the amount of Blue dye adsorbed from mixture dyeing varies with the sort and the concentration of its partner dye and with the dyeing temperature was discussed from the standpoint of the instability constant and the affinity.

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Chemical Behaviors of the Intermediates Produced during the Reductive Photobleaching of Eosin in the Evacuated Alcoholic Solution

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One of the present authors (Koizumi) and Imamura[1] investigated kinetically the photobleaching of eosin in the deaerated ethanol solution and concluded that the reaction proceeds via the following primary processes:

$$D \xrightarrow{h\nu} D^* \qquad \text{(i)}$$

$$D^* \rightarrow D^t \qquad \text{(ii)}$$

$$D^t + RH \rightarrow DH\cdot + R\cdot \qquad \text{(iii)}$$

$$(DH\cdot \rightarrow \text{final products})$$

Where D: dye ion; D^*: singlet excited state of dye (S^*); D^t: triplet state of dye (T); RH: ethanol; DH·: semiquinone of eosine; R·; radical produced from ethanol.

Now, in order to make clear the details of these elementary reactions, it is essential to study about the chemical behaviors of the intermediates, D^t and DH·. Experiments by the flash technique have already been commenced in the authors' laboratory. However, the ordinary kinetic studies, for example, the investigation about the effect of added substances on the reaction rate are expected to be useful for this purpose to some extent. In the present research, isopentane, *n*-hexane, benzene, cyclohexene, *n*-hexene and cyclooctatetraene (COT) were added to the reaction system and the variation of the rate of photobleaching was examined.

1) M. Koizumi and M. Imamura, This Bulletin, **28**, 117 (1955); **29**, 899 (1956); M. Imamura, ibid., **30**, 249 (1957).

Experimental

Materials.—*Eosine.*—Grübler's product was used. Stock solution 1×10^{-4} M was kept in the dark and this was diluted to 1×10^{-5} M for each experiment. Isopentane, *n*-hexane and benzene were purified by the usual methods. COT prepared kindly by Dr. N. Hagiwara of Osaka University, was further distilled under vacuum three times and was stored in an evacuated ampule.

n-Hexene-2 and cyclohexene of Tokyo Kasei were distilled two or three times and were reserved in vacuo.

Ethanol, after being treated with concentrated sulfuric acid, was made free from aldehyde by the addition of silver oxide and dehydrated by calcium oxide.

Apparatus and Procedures.—A tungsten projection lamp (75 V. 500 W.) was used as a light source. The voltage was fixed at 45.0 ± 0.5 V. and the intensity was checked by measuring the bleaching rate of the aqueous eosine solution (not deaerated) throughout all the experiments[1]. A yellow glass filter cutting off < 450 mμ and a reaction cell was attached to the metallic case surrounding a glass tube, 6 cm. in diameter, in which the lamp was placed. Degassing of the sample was performed carefully by repeating the vacuum distillation. A Terrex cell for measuring the absorption spectra was used as a reaction vessel, the upper part of which was fused to a tube of hard glass for the cell to be attached to the

above distillation set. After the deaerated sample was poured into the cell it was fused off at a suitable position. The sample was irradiated in a thermostat usually at 25°C and at suitable time intervals the absorption spectra were measured by a Hitachi spectrophotometer (EPU-2A). The measurement of fluorescence spectra was done by the fluorescence attachment of the spectrophotometer.

Results

Rate Formula.—Throughout all the experiments, the absorption spectra of the irradiated solution gradually declined keeping the same shape and particularly with the maximum at the same position as in the original solution. The situations are exactly the same as in the case of the pure alcoholic solution of eosine[1]. One example is shown in Fig. 1.

The rate of bleaching can be expressed by the same formula presented by Koizumi and Imamura[1],

$$-\frac{dc}{dt}=\frac{k}{d}I_0(1-e^{-\alpha cd})\times 10^3 \qquad (1)$$

where c is the concentration of dye in mol./l., I_0 the intensity of illuminating light (mol. cm^{-2} sec^{-1}), α the average or effective molar absorption coefficient and d the thickness of the solution in cm.

Integrating Eq. 1, one obtains

$$\ln(e^{\alpha c_0 d}-1)-\ln(e^{\alpha cd}-1)=10^3 kI_0\alpha t \qquad (2)$$

By using the properly determined value of α, one can obtain k from the inclination of the linear plot of $\ln(e^{\alpha cl}-1)$ against t.

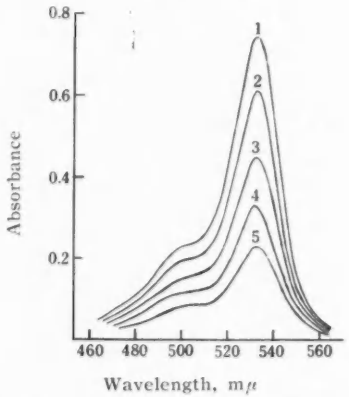

Fig. 1. The absorption spectrum of the irradiated solution of eosin in ethanol with 25% isopentane.
1. initial
2. 10 min.-irradiation
3. 20 min.-irradiation
4. 30 min.-irradiation
5. 40 min.-irradiation

The Effect of the Added Substance.—*a) Isopentane, n-hexane, benzene and COT.*—The addition of these substances does not affect appreciably the absorption spectra of eosin in the visible region nor the fluorescence spectra. In the case of high concentration there is a slight decrease

TABLE I

Isopentane		*n-Hexane*	
Mole fraction	$k\times10^4$	Mole fraction	$k\times10^4$
0.334	1.18	0.309	2.55
0.143	2.53	0.130	2.87
0.100	2.74*	0.0731	3.84
0.0814	4.86	0.0472	4.36
0.0529	4.94	0.0230	3.82
〃	3.80*	0	4.30**
0.0254	5.66		
0	5.82**		

Benzene		*Cyclooctatetraene*	
Mole fraction	$k\times10^4$	Mole fraction $\times10^5$	$k\times10^4$
0.220	1.23	650	0
0.141	1.27	65	0.532
0.0681	1.38	32.2	0.841
0.0334	1.41	8.07	1.22
0.0167	1.67	5.26	1.93
0.00269	2.10	0	1.97
0	1.85		

* Isopentane purified with utmost caution.
** In these two runs, k-value in the pure alcoholic solution is markedly different from that of the other runs (including those in Table II). The cause for this is unknown though it may perhaps be due to the pretreatment of alcohol employed. The effect of the added substance will certainly not be affected seriously by this, since it is essentially related with a relative quantity to the reference alcohol.

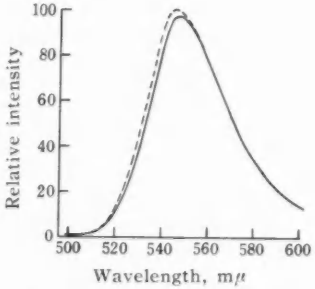

Fig. 2. The effect of addition of isopentane on the fluorescence of eosin.
—— 25% isopentane
------ without isopentane

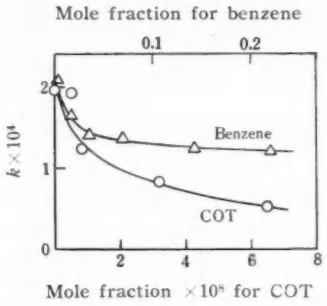

Fig. 3. Plot of k against the concentration of COT and benzene.

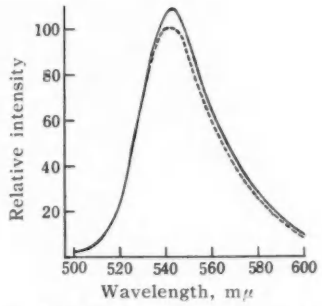

Fig. 4. The effect of addition of cyclohexene on the fluorescence of eosin.
—— 5% cyclohexene
------ pure alcohol

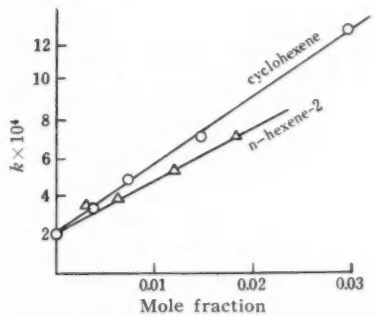

Fig. 5. Plot of k against the concentration of the added substances.

TABLE II

Cyclohexene		*n-Hexene*	
Mole fraction	$k\times10^4$	Mole fraction	$k\times10^4$
0.0295	12.8	0.0181	7.25
0.0146	7.07	0.0119	5.39
0.00726	4.87	0.00593	3.98
0.00362	3.42	0.00296	3.48
0	1.97	0	2.18

in the fluorescence intensity. As an example, the influence of the addition of isopentane upon the fluorescence spectra is shown in Fig. 2. Other substances show more or less similar effects. In Fig. 3 rate constants k's are plotted against the concentration and the data are given in Table I. It is apparent that the above four substances have a retarding effect and among them, COT is by far the most significant inhibitor for the bleaching reaction.

b) n-Hexene and cyclohexene.—Neither absorption spectra nor the fluorescence intensity is affected essentially. At higher concentration, the intensity of fluorescence increases slightly as shown in Fig. 4. The values of k are plotted against mole fraction in Fig. 5, which shows that k linearly increases with the concentration of the added substance. The data are given in Table II.

Discussion

The primary processes were already described in the introduction. The fate of DH· and R· is not yet quite certain but the effect of the added substance on the rate is expected to be due to their interference with one of the above three steps i—iii. Since the mechanism would naturally be different for two groups, the retarding substances (isopentane, *n*-hexane, benzene and COT) and the promoting substances (*n*-hexene and cyclohexene), they will be considered separately.

The Retarding Effect.—Since either the absorption spectrum or the intensity of fluorescence is scarcely affected by the addition of the retarding substances, the first two processes in these systems have a rate almost equal to what they have when they are not added. Hence the remaining process iii ought to be eventually retarded by the interference of the added substance. There are two possibilities to be considered for this; the one is the deactivation of D^t and the other is the recovery of D by the removal of hydrogen from DH·. But the latter possibility may safely be ignored from the fact that the above retarders have no tendency to be hydrogenated or scarcely any. Hence the conclusion is that the triplet state of eosin is deprived of its excess energy by the added substance, resulting in the decrease of the bleaching rate. Thus the only process which must be taken into account is the following one

which competes with process iii,

$$D' + Q \rightarrow D + Q \qquad k_Q[Q] \qquad \text{(iv)}$$

where Q represents an added retarder.

Assuming the steady-state concentration for D* and D' one can write for k the following:

$$k = \varphi_{S\rightarrow T} \frac{k_a[RH]}{k_a^S[RH] + k_Q[Q]} \qquad (3)$$

where $\varphi_{S\rightarrow T}$ gives the fraction of the singlet state going to the excited triplet, k_a is the rate constant for the effective hydrogenating reaction iii, k_a^S, the sum of the rate constants for the genuine reaction and the deactivation of D' by alcohol. From Eq. 3

$$\frac{1}{k} = \frac{1}{\varphi_{S\rightarrow T}} \frac{k_a^S}{k_a} + \frac{1}{\varphi_{S\rightarrow T}} \frac{k_Q[Q]}{k_a[RH]} \qquad (4)$$

Thus, the plot of $1/k$ against $[Q]/[RH]$ gives a straight line as shown in Fig. 6. From the inclination $k_Q/\varphi_{S\rightarrow T}k_a$ and the intersect with the ordinate $\left(\frac{1}{\varphi_{S\rightarrow T}} \frac{k_a^S}{k_a}\right)$, one can easily evaluate a value of k_Q/k_a^S, which gives a measure for the efficiency of the added substances in deactivating D'. The results are shown in Table III.

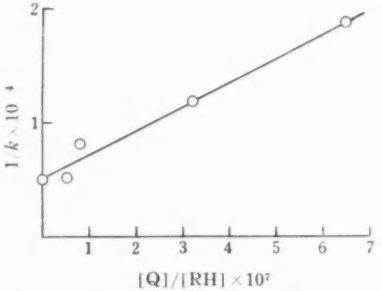

Fig. 6. Plot of $1/k$ against $[Q]/[RH]$ where Q is cyclooctatetraene.

TABLE III. THE KINETIC DATA FOR THE RETARDING SUBSTANCES

Retarder	$k_Q/\varphi_{S\rightarrow T}\cdot k_a$	$k_a^S/\varphi_{S\rightarrow T}\cdot k_a$	k_Q/k_a^S
Isopentane	5.0×10^3	1.7×10^3	2.9
n-Hexane	4.4×10^3	2.4×10^3	1.9
Benzene	3.4×10^4	5.4×10^3	6.3
COT	2.0×10^{10}	5.5×10^3	3.7×10^6
Water			0.053[1]

It is interesting that saturated hydrocarbons which are chemically inactive are rather better deactivators than water. The value for COT is enormously large, the result being consistent with that of Schenck[2]. It may be that the electronic excess energy can effectively be transferred to the vibrational energy of COT which has various modes of bending and torsion due to the nonplanarity of its structure.

The Promoting Effect. — Cyclohexene and *n*-hexene, which promote the bleaching rate have a single double bond. These two substances also give scarcely any influence on the absorption spectrum and fluorescence intensity of eosine, so that they do not have much effect upon the rate of processes i and ii. Furthermore in view of their promoting effect, their action on the T-state of the dye is not thought to be an essentially deactivating one. At first sight, the promoting action might be attributed to the same kind of reaction between D and the added substance (P) as that between D and alcohol represented by iii. But if so, it is very curious that COT, which is exceedingly unsaturated, shows a quite opposite effect. Moreover, since much of the deactivating process would certainly occur along with the genuine reaction (dehydrogenation of P), the overall rate constant k should be represented as follows:

$$k = \varphi_{S\rightarrow T} \frac{k_a[RH] + k_P[P]}{k_a^S[RH] + k_P^S[P]} \qquad (5)$$

where $k_P[P]$ refers to the rate of reaction leading to bleaching and $k_P^S[P]$ is the sum of $k_P[P]$ and that for the deactivating process. Eq. 5 never gives linearity between k and $[P]$ since $k_P^S[P]$ most certainly can not be neglected in view of the rather large value of $k_P[P]$.

Thus, it seems that a plausible interpretation can never be given on the basis of the reaction scheme presented by Koizumi and Imamura[1].

Now, according to the unpublished results for the bleaching reaction of eosine in alcohol by the flash-technique which have been obtained in the authors' laboratory[3], there are two intermediates spectroscopically observed, other than D', and these have different durations though in the same order of magnitude (few millisec.).

As another intermediate besides semiquinone, the most probable one would be a certain kind of intermolecular complex between D' and RH, or alternatively, (DH·.....R·) trapped in the same cage. In either case the introduction of another

2) G. O. Schenck and K. Kinkel, *Naturwissenschaften*, **38**, 355 (1951).
3) To be published in the near future.

intermediate of this kind modifies the reaction scheme in such a manner that process iii must now be divided into the following ones,

$$D^{t} + RH \rightarrow X \qquad (iii')$$

$$X \rightarrow D + RH \qquad (iii'')$$

$$X \rightarrow DH\cdot + R\cdot, \quad k_X \qquad (iii''')$$

where X represents either the complex between D^t and RH, or DH· and R· exisitng in the same cage.

In view of a small quantum yield of photobleaching, a large part of X would perhaps decompose into D and RH (process iii'') resulting only in the dissipation of excess energy of D^t, while a small fraction of X would complete the bleaching reaction by step iii'''. It is of course undecided whether X is some kind of molecular complex or a transient state in which DH· and R· exist in the same cage, but the two alternatives give exactly the same kinetics.

Now, if one modifies the reaction scheme as above, one can interpret quite rationally the promoting action of the added substance. Thus, if the added substance P attacks X in such a manner that it detaches the R-part from the latter, producing a more stable radical PR· and leaving behind a metastable DH·, then the rate of bleaching would be increased. This type of attack may perhaps be so specific that it would not be accompanied with much of the deactivating process. The process can formally be written as follows:

$$X + P \rightarrow DH\cdot + RP\cdot \qquad (v)$$

Taking into account iii', iii'', iii''' and v instead of iii, one can give the expression for k as follows:

$$k = \varphi_{S\rightarrow T}\varphi_{T\rightarrow X}\frac{k_X + k_P[P]}{k_X^S + k_P[P]} \qquad (6)$$

where k_X^S is the sum of the rate constants for reaction iii'' and iii'''. If one assumes that the action of P on X consists mainly of reaction v and is not of such a nature as to promote reaction iii'' and moreover that $k_X^S \gg k_P$ holds as already discussed above, then Eq. 6 is approximately rewritten as

$$k = \varphi\frac{k_X + k_P[P]}{k_X^S} \qquad (\varphi = \varphi_{S\rightarrow T}\varphi_{T\rightarrow X}) \qquad (7)$$

which explains the linear relationship between k and [P] experimentally obtained. From the plot of k against [P], one can evaluate the values of k_X/k_P, which are shown in Table IV.

TABLE IV. THE KINETIC DATA FOR THE PROMOTING SUBSTANCES

Promotor	Inclination	Intersection	k_P/k_X
Cyclohexene	21.4×10^{-4}	2.15×10^{-4}	10.0
n-Hexene-2	15.3×10^{-4}	2.50×10^{-4}	6.1

It is to be added that the same relation as Eq. 7 would be obtained, if P attacks D^t in such a specific manner as to produce DH· far more rapidly than to dissipate the excess energy in vain. A relation similar to Eq. 4 would also be obtained for retarding substances if one assumes that X instead of D^t is selectively decomposed by Q into D and RH·. But the assumption is highly improbable that the retarding substances and the promoting substances attack the same one molecular species in a quite different and peculiar fashion. A more natural picture would be that the two groups of the added substances act on different molecular species in a different way as described above. Of course, in order to make the above remark more definitely, it is necessary to study further about the chemical behavior of D^t, X and DH· toward many other substances and especially to use the flash technique.

Summary

The effect of the addition of isopentane, *n*-hexane, benzene, cyclohexene, *n*-hexene and cyclooctatetraene was examined upon the rate of the reductive photobleaching of eosine in the evacuated alcoholic solution. It was found that the saturated hydrocarbons, benzene and COT retard the reaction more or less, COT being most prominent in its effect, while the hydrocarbons with a single double bond (cyclohexene and *n*-hexene) act, contrary to the authors' expectation, as the promotors of the bleaching. The retarding effect of the first group was interpreted to be due to the deactivation of the T-state of dye ion by the added substances, but the promoting action of the second group could not be accounted for rationally on the basis of the above scheme. To fit the present results, therefore, a modified scheme was newly proposed in which a certain kind of molecular complex between D^t and RH is formed prior to DH·.

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Molecular Structure of Acrylonitrile by Electron Diffraction

By Takahide SAITO and Takeshi UKAJI*

(Received July 20, 1959)

The shortening of a single bond between two multiple bonds has been studied in various cases[1], but not yet in the cases with the structure,

$$C{=}C{-}C{\equiv}N$$

The authors wish to report some results on acrylonitrile (Fig. 1) by the electron diffraction.

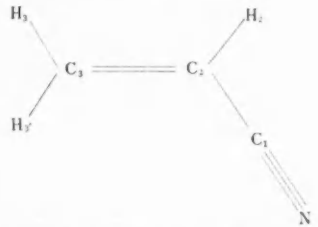

Fig. 1. Molecular scheme of acrylonitrile.

Experimental

The apparatus of electron diffraction is the same as in the previous reports from the authors' laboratory[2], with the exception of the use of two camera lengths, 9.1 and 10.1 cm. The electron wavelength, about 0.055 Å, was calibrated by gold foil diffraction.

The sample is kindly supplied to the authors' by Professor S. Kambara, b. p. −78°C.

Measurements were carried out by the usual visual method.

Procedure and Results

The experimental visual curve from eight photographs is shown in Fig. 2. The dotted line for $q>80$ means less accurate observation due to the obscurities of photographs and that for $q<10$ is an assumed line to help the calculation of the radial distribution curve.

The radial distribution curve has been calculated from the visual intensity curve according to the equation[3],

$$r\cdot D(r)=\sum_{q=1,2\cdots}^{q_{max}} I(q)\exp(-aq^2)\sin \pi/10\cdot qr$$

$$q=(4\pi/\lambda)\sin(\theta/2)$$

$$\exp(-aq^2_{max})=0.1$$

in which θ is the scattering angle, and λ is the wavelength of the beam. The curve obtained shows the still remaining ghosts. However, it is convenient to assign each peak in this curve for the following trial and error method.

The first peak of 1.16 Å is attributed to the C≡N bond from the consideration of weight**. The second peak of 1.38 Å corresponds to the overlapped contribution of C=C and C−C bonds. The peaks at 2.12 and 3.46 Å correspond to the interatomic distances of nonbonded C···H and C···N, respectively.

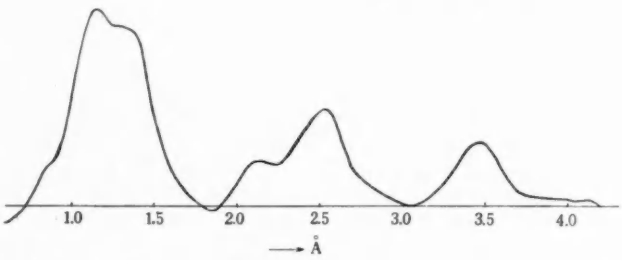

Fig. 2. Radial distribution curve.

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1) For example, see the following tables: L. E. Sutton and P. W. Allen, *Acta Cryst.*, **3**, 46 (1950); H. Oosaka, "Kagaku Jikkengaku", Vol. 5, Kawade-Shobo, Tokyo (1943), p. 325; Y. Morino, K. Kuchitsu and Y. Hirota, "Jikken Kagaku Koza", Vol. 3, Maruzen Co., Ltd., Tokyo (1958), p. 241. The data for some molecules are given in Table III.

2) T. Yuzawa and M. Yamaha, This Bulletin, **26**, 414 (1953).

3) V. Schomaker et al., *J. Am. Chem. Soc.*, **64**, 2693 (1942).

** The term "weight" means the value of nZZ/r for each interatomic distance, where n is the number of the same interatomic distance r and Z is the atomic number.

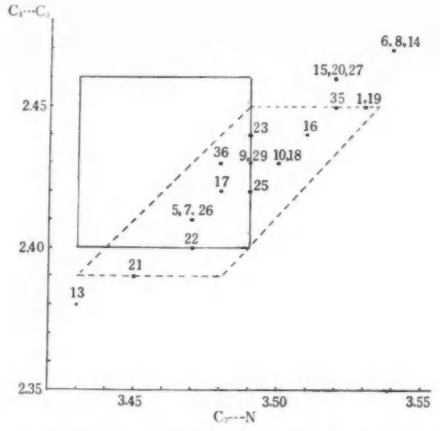

Fig. 3. The parameter chart of $C_1\cdots C_3$ vs. $C_3\cdots N$.

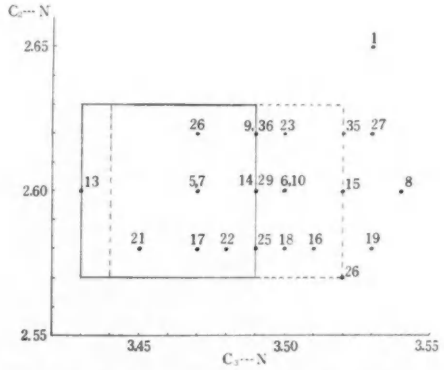

Fig. 4. The parameter chart of $C_2\cdots N$ vs. $C_3\cdots N$.

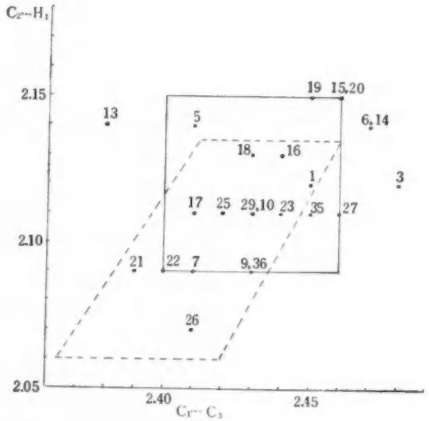

Fig. 5. The parameter chart of $C_2\cdots H_1$ vs. $C_1\cdots C_3$.

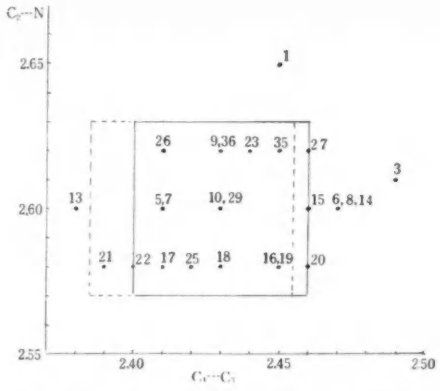

Fig. 6. The parameter chart of $C_2\cdots N$ vs. $C_1\cdots C_3$.

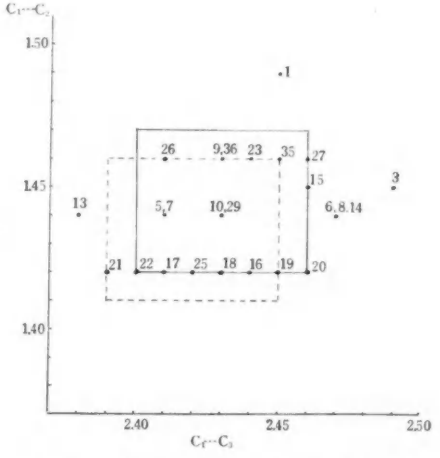

Fig. 7. The parameter chart of $C_1\cdots C_2$ vs. $C_1\cdots C_3$.

The theoretical intensity curve for assumed models has been calculated by the use of the equation[3]

$$I(q)=\sum_{ij}(Z_iZ_j/r_{ij})\exp(-a_{ij}q^2)\sin \pi/10\cdot qr_{ij}$$

$$a_{ij}=(\pi^2/200)l_{ij}$$

where r_{ij} is the distance between the i-th and j-th atom, Z_i is the atomic number of i-th atom and l_{ij} is the mean amplitude of r_{ij}.

The coefficient of thermal vibration, a_{ij}, is roughly estimated with reference to the calculated data [4-6]. The coefficients used

4) J. Karl, *J. Chem. Phys.*, **20**, 65 (1952).
5) Y. Morino, K. Kuchitsu and T. Shimanouchi, ibid., **20**, 726 (1952).
6) Y. Morino, K. Kuchitsu, A. Takahashi and K. Maeda, ibid., **21**, 1927 (1953).

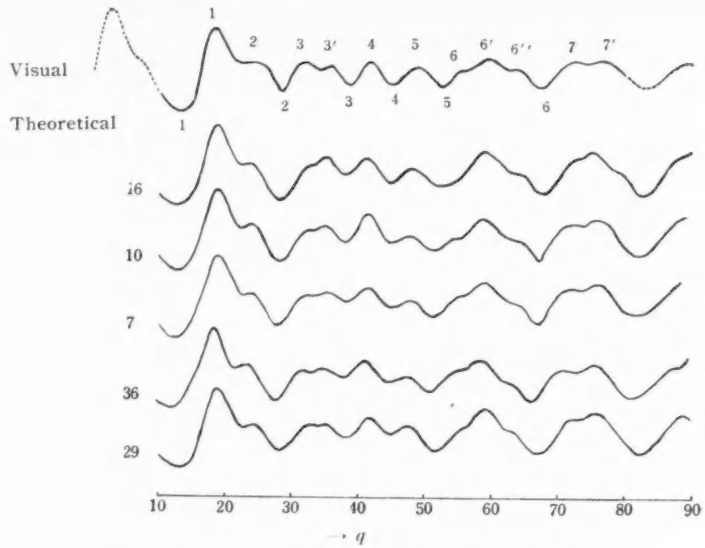

Fig. 8. Theoretical curves and visual curve.

TABLE I. THE COEFFICIENTS OF THERMAL VIBRATION

Atomic pair	a	Atomic pair	a
C—H	0.00028	H···C_1	0.00013
C=C	0.00005	C_2···N	0.00006
C—C	0.00008	C_3···N	0.00012
C≡N	0	H_3···N	0.00032
H_3···C_2	0.00039	H_2···N	0.00011
C_3···Cl	0.00016		

TABLE II. THE COMPARISONS WITH EACH MODEL

Atomic pair	I	II	III	IV	V
C—C	1.42	1.44	1.44	1.46	1.44
C≡N	1.16	1.16	1.16	1.16	1.16
C_1···C_3	2.44	2.43	2.41	2.43	2.43
C_3···N	3.51	3.50	3.47	3.49	4.49
C_2···N	2.58	2.60	2.60	2.58	2.60
Average of $q_{calcd.}/q_{obsd.}$	0.995	0.992	1.000	0.996	0.995
Root mean deviation	0.014	0.015	0.017	0.013	0.017

The length of atomic pair is given in Å unit.

are shown in Table I. The theoretical curve was calculated to cover the following ranges of parameters, $C_3{\equiv}N$ 1.16, $C_2{=}C_3$ 1.42~1.46, $C_1{\cdots}C_3$ 2.41~2.47 and $C_3{\cdots}N$ 3.46~3.53 Å. In the above calculations, Z_H 1.25 and C—H 1.08 Å were used and each term of H···H was neglected. The theoretical curves, agreeing well with the visual intensity curve and having the values of parameters close to the interatomic distances obtained from the radial distribution curve, are shown in Fig. 2.

In Table II are shown the values of principal parameters in these models. Although these models are more appropriate rather than the others, the agreements with the visual curve are not sufficiently satisfactory. For example, there are considerable disagreements in the following aspects: (1) the relationships of intensity of max. 3 and 3′, (2) the relative intensity of max. 7 and 7′, (3) the location of min. 5 (the experimental has larger q than all the theoreical), (4) the relationships of intensity of max. 6, 6′ and 6″. Therefore, it is difficult to prefer a model to the other form. However, the following ranges for the parameters may be supported in reference to values of the similar molecules (Table III), C≡N 1.15~1.17, C=C 1.32~1.36, C—C 1.42~1.46 and $C_1{\cdots}C_3$ 2.41~2.44 Å. The difficulty in determining the best model may be the result of the uncertain observation of intensity, especially in the range of larger q values.

However, it is probable from the considerations of the parameter charts that the molecule of acrylonitrile has the following interatomic distances:

C≡N	1.16±0.01 Å
C=C	1.34±0.02 Å
$C_2{\cdots}C_3$	2.43±0.02 Å
C—C	1.44±0.02 Å

TABLE III. THE INTERATOMIC DISTANCES (Å UNIT) OF SIMILAR COMPOUNDS

Molecule	Atomic pair C≡N	C—C	C=C	C≡C	Method	Ref.
H—CN	1.156				M. W.*	1
CH_3·CN	1.157	1.458			M. W.	2
	1.16	1.49			E. D.**	3
CN·CN	1.16	1.37			E. D.	3
CH_2=CH·CH=CH_2		1.46	1.35		E. D.	3
		1.47	1.37		S. P.***	4
CH_3C≡C·CH_3		1.47		1.20	E. D.	3
CH≡C·C≡CH		1.36		1.19	E. D.	3
CH≡C·CN	1.157	1.382		1.203	M. W.	1
CH_3·C≡C·CH=CH_2		1.42	1.35	1.20	E. D.	6
		1.47				

* M. W.; Microwave spectrum.
** E. D.; Electron diffraction.
*** S. P.; Infrared spectrum.

1) W. Gordy et al., *Phys. Rev.*, **86**, 1055 (1952).
2) L. F. Thomas et al., *Trans. Faraday Soc.* **51**, 619 (1955).
3) L. Pauling and L. O. Brockway, *J. Am. Chem. Soc.*, **61**, 927 (1939).
4) O. Bastianssen; these values were quoted from Sutton's Table., L. E. Sutton and P. W. Allen, *Acta. Cryst.*, **3**, 46 (1950).
5) A. A. Westenberg et al., *J. Am. Chem. Soc.*, **72**, 199 (1950).
6) V. Schomaker, *J. Am. Chem. Soc.*, **64**, 2693 (1942).

A further investigation about the structure of this molecule by the use of electron difraction sector microphotometer method will be given in succeeding paper***.

*** During the preparation of this paper the authors read the following paper regarding the molecular structure of acrylonitrile; C. C. Costain and B. P. Stoiceff, *J. Chem. Phys.*, **30**, 777 (1959), which reported the following values about the interatomic distances, C≡N 1.1637, C–C 1.4256 and C=C 1.338$_9$ Å, by the use of microwave spectroscopy. The author's results are very near to their values.

The authors have great pleasure in acknowledging their debts of gratitude to Professor A. Kotera and Professor K. Suzuki for their continued encouragement and advice and to Dr. K. Kuchitsu for his help with the calculation.

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*Determination of Reducing Sugars by Means of Back Titration against Alkaline Copper Solution. I**

By Masahito TAKAHASHI

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Since the determination by means of Fehling solution has become used so generally for sugar analysis, different chemists have devised, in consequence of its importance in both practice and research, so many modifications that there is probably no method in analytical chemistry which suffers more from variety of procedure. Numerous modifications have been described which differ in analytical details. Fehling solution is rather unstable, so efforts have been made to improve its stability, and to establish a simpler and more practical procedure.

The amount of copper which is reduced by various sugars has been found to vary according to the alkalinity, the temperature, the rate of ebullition, the time of heating, the type of tartrate, the amount of contact with air, etc. Among them the most important variables are the temperature, the time of heating, and the rate of ebullition. Consequently some methods have devised for heating because it is difficult to standardize the temperature and the rate of ebullition. The indirect heating is frequently employed as in the case of Main's pot method where the temperature is regulated by a boiling water bath and the reduction is carried out in a test tube provided with floats. But this is not a fine procedure, because it requires a complicated operation and demands skilfulness in analyst. Then, the results should be corrected according to the variation of variables rather than a strict standardization of the reacting condition is demanded. Blank titration with a standard sugar solution, which checks the variation of conditions and corrects the results, is most suitable for the present purpose.

Numerous procedures already devised for the determination of the quantity of reduced copper can briefly be divided into a partial reduction method and a total reduction method. In the former a certain volume of Fehling solution is brought into a reaction with a given amount of sugar which does not reduce all the copper, and the cuprous oxide produced is weighed directly or estimated by means of redox titration. The other is a method which, in principle, involves the determination of the volume of sugar solution required to reduce completely a measured volume of alkaline copper solution, the end point being indicated by a spot test or an internal indicator. This is indeed one of the earliest procedures for the determination of the reducing power. Soxhlet heated a known volume of Fehling solution to boiling in an open dish and added the sugar solution until the copper was completely reduced. No great accuracy was possible by this procedure, even in highly skilled hand. The degree of accuracy of this method was considerably increased by various devices, namely, by boiling the solution in a flask instead of an open dish, to diminish back-oxidation, and by using a suitable indicator. Lane and Eynon[1] found that the end point was internally indicated by the reduction of methylene blue to methylene white by minute excess of reducing sugar and determined the weight of each sugar required to reduce the copper completely. These weights, which varied with nature of sugar and with its concentration, constituted their table for analysis. This method, described as "the most convenient, most expeditious, and frequently the most accurate method"[2], has been adopted for industrial and scientific purposes, but seems still to be a complicated and time-consuming procedure with some disadvantages. For instance, it consumes a large volume of sugar solution, and is not available for the determination of a small quantity of sugar, etc.

In general, the total reduction method,

* Partly presented at the Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1957.

1) J. H. Lane and L. Eynon, *J. Soc. Chem. Ind. (London)*, **42**, 32T, 143T (1923); **44**, 150T (1925); **46**, 434T (1927).

2) F. J. Bates et al., "Polarimetry, Saccharimetry and the Sugars", U. S. Government Printing Office, Washington (1942), p. 185.

represented by Lane and Eynon's method, is simpler, more practical, and more accurate than the partial reduction method, represented by the gravimetric method and Bertrand's method. In view of this advantageous quality, the author has endeavored to improve the former procedure and to establish a more convenient method of procedure with a high accuracy on such a way as to confer the maximum possible simplicity of procedure and to eliminate the personal factor as far as possible. To this end a back titration method has been devised.

Experimental

Materials.—The following substances were used for the present investigation. An anhydrous glucose was obtained by recrystallizing a commercial glucose (monohydrate, the Japanese Pharmacopoeia) from water and acetic acid. A pure commercial lactose was recrystallized from water. A pure commercial galactose was recrystallized from water and alcohol. Crystalline copper sulfate ($CuSO_4 \cdot 5H_2O$) of reagent grade was recrystallized from water. A 50% solution of sodium hydroxide (reagent grade) was prepared and allowed to stand until a precipitate of sodium carbonate appeared. By filtering it through asbestos a clear solution was obtained. Benzoic acid, Rochelle salt and methylene blue were all of reagent grade.

Reagents. — *I) Standard sugar solution.* — One gram of crystalline benzoic acid and 2.046 g. of crystalline glucose were dissolved in water and made up 1 l. with water.

II) Copper solution.—Sixty-six grams of caystalline copper sulfate was dissolved in water and made up to 1 l. with water.

III) Alkaline solution.—The calculated amount of sodium hydroxide solution containing 110 g. of sodium hydroxide and 345 g. of Rochelle salt were dissolved in water and made up to 1 l. with water.

IV) Indicator.—Half a gram of methylene blue was dissolved in 100 ml. of water.

Procedure. — In Soxhlet's method, Lane and Eynon's method and others, a measured volume of the boiling alkaline copper solution is titrated with a sugar solution, the end point being indicated by a spot test or an internal indicator, and the concentration of the sugar solution is estimated from the volume of the sugar solution required to reduce the alkaline copper solution completely. On the other hand, in this back titration method a boiling mixture of a measured volume of the alkaline copper solution and a measured volume of the sugar solution is back-titrated with the standard sugar solution, and the concentration of the sugar solution is estimated from the volume of the standard sugar solution required to reduce the mixture completely.

It is well known, for example, that if the sugar solution is added in portions 5 ml. and the liquid boiled for 10 sec. after each addition, the total volume required will not be exactly the same as if the whole of the sugar solution is added at once. Now in this method nearly the whole of the standard sugar solution is added at once and after boiling the rest quantity is added (normal titration). As in the Lane and Eynon's method, a preliminary titration system is adopted, by which the required volume of the standard sugar solution is found approximately in order that almost the whole of it may be added at one time simultaneously with heating. In the case of the blank titration the required volume is known approximately, so that a preliminary titration is unnecessary.

In a blank titration, a mixture of 20 ml. of water and 10 ml. of an alkaline copper solution is titrated with the standard sugar solution. In the normal titration, the volume of the standard sugar solution can be obtained, which is required to reduce a mixture of the alkaline copper solution (10 ml.) and 20 ml. of the sugar solution. The difference between the two quantities obtained thus represents the concentration of the sugar solution.

a) Blank titration.—Equal volumes of solutions II and III are mixed thoroughly. Ten milliliters of the mixed solution and 20 ml. of distilled water are measured into a 100~300 ml. flask and heated over an asbestos wiregauze with a 300~500 W. electric heater charged full voltage. About 23.5 ml. of the standard sugar solution delivered from a 25 ml. burette is added into the flask as soon as possible. For this purpose an automatic burette is very convenient, the outlet of which is connected by melting with a glass tube (about 10 cm.) bent twice at right angles so that the solution in the burette is not heated by the reaction mixture. After the liquid has begun to boil vigorously, it is kept in moderate ebullition by lowering the working voltage. After boiling for two minutes, 3 to 6 drops of the methylene blue indicator are added, and the standard sugar solution is added in small quantities, that is to say, several drops or less at a time, and after the commencement of decolorization, drop by drop. The liquid is boiled for about ten to fifteen seconds between successive addition, and the titration is continued until the color of the indicator is discharged. The titration is completed in about one minute, so that the reaction liquid is boiled altogether for 3 min. without interruption. The decolorization of the methylene blue is easily detected, since the blue color of copper ion has already vanished. The rate of heating is regulated carefully so as to make the precipitate as much as possible. The end point can be determined with accuracy of less than one drop of the standard sugar solution. At the end point the blue color of the methylene blue vanishes suddenly, and the faint purple tint is still observable. The methylene white is rapidly reoxidized by air, particularly at the high alkalinity of this reaction mixture. Hence it is essential that air is excluded during the titration.

This is accomplished by making an uninterrupted current of steam issue from the neck of the flask on which the analysis is performed.

So long as solutions II and III are mixed correctly, the titer of the blank titration is constant; so that the blank titration is unnecessary at each time of mixing. When the sample solution contains materials other than sugars to be determined, a blank titration should be made against the solution containing these materials.

b) Preliminary titration.—Ten milliliters of the mixed copper solution is boiled in a 100~300 ml. flask after adding 20 ml. of the sample sugar solution. Usually after ten seconds of ebullition the reduction of the copper solution is nearly completed, which can easily be seen from the disappearance of the blue color of cupric ion and the bright red color imparted to the boiling liquid by the suspended cuprous oxide. If it is judged that nearly all the copper has been reduced, boiling is continued for about one minute from the beginning of ebullition, 3 to 5 drops of the methylene blue indicator are added, and then the standard sugar solution is added in small quanties, that is to say, 0.2 ml. or less at a time at regular intervals, the liquid being allowed to boil, until the color of the indicator is discharged. When unreduced copper is still found to be there in large quantity after boiling a mixture of 20 ml. of the sample solution and the copper solution about ten seconds, 3 ml. of the standard sugar solution is added and the whole is allowed to boil for ten seconds and so on, until it is considered unsafe to add a further large increment of the standard sugar solution. Boiling is continued further thirty seconds, after which the indicator is added and the titration is completed by small additions of the standard sugar solution as already mentioned. The indicator should not be added until the end point is nearly reached.

When maximum accuracy is not required, a single preliminary titration gives satisfactory results; the error will, as a rule, not exceed 0.6 mg. per 20 ml. of the sample solution.

c) Normal titration.—Ten milliliters of the mixed copper solution and 20 ml. of a sample sugar solution are measured into a 100~300 ml. flask, and, as soon as the mixture is heated, almost the whole of the standard sugar solution is added, which required to reduce all the copper, so that if possible not more than 1 ml. is required later to complete the titration. The approximate volume of the standard sugar solution required is estimated by a preliminary titration. After the liquid has begun to boil, it is kept in moderate ebullition for 2 min., and then 3 to 6 drops of the methylene blue indicator are added, and the titration is then completed in 1 min.

Results

The author has measured the volume of the standard sugar solution required to reduce a mixture of 10 ml. of the alkaline copper solution and 20 ml. of water (*blank titration*), and that of the standard sugar solution required to reduce a mixture of 10 ml. of the alkaline copper solution and 20 ml. of the solution of sugars of various concentrations (*normal titration*). The relationship among the weight (W) of sugar in mg. in 20 ml. of sugar solution, the volume (B) in ml. of the standard sugar solution required in the blank titration, and the volume (m) of the standard sugar solution in the normal titration, has been found to be;

$$W = 2(B-m)tf$$

where t is a correction term, and f is a factor of the standard sugar solution.

For the purpose of calculating the weight of sugar from difference ($B-m$), a correction term t has been introduced, which varies with the nature of the sugar and the term ($B-m$). The term t is 1.000 over widely different concentrations, viz. from 1 to 48 mg. per 20 ml. in the case of glucose, but in case of lactose and galactose it varies with the difference ($B-m$), the values of which are shown in Table I.

In the titrations on which Table I is based, the volume of the standard sugar solution added to the reaction mixture after heating was about 0.3~0.5 ml. less than the total volume required, and during the last third minute of ebullition, this complementary quantity was added, two

TABLE I. "t" OF LACTOSE AND GALACTOSE

$B-m$, ml.	Lactose	Galactose
1	1.32	1.03
2	1.32	1.03
3	1.32	1.03
4	1.32	1.03
5	1.32	1.03
6	1.32	1.03
7	1.318	1.030
8	1.315	1.031
9	1.314	1.031
10	1.312	1.032
11	1.310	1.032
12	1.309	1.032
13	1.308	1.032
14	1.307	1.033
15	1.307	1.033
16	1.307	1.033
17	1.306	1.034
18	1.306	1.034
19	1.036	1.034
20	1.306	1.034
21	1.306	1.034
22	1.305	1.035
23	1.305	1.035
24	1.305	1.035

TABLE II. EXAMPLES

Reducing sugar contained	Weight of reducing sugar in solution mg./20 ml.	Material mixed	B (ml.) required in blank titration	m (ml.) required in normal titration	f factor	t correction term	$2(B-m)ft$ weight of reducing sugar determined mg./20 ml.
Glucose	44.64	no	24.30	2.45	1.021	1.000	44.62
Lactose	45.66	no	23.98	7.30	1.047	1.307	45.64
Glucose	38.18	Sucrose 20 g./100 ml.	20.60	1.90	1.021	1.000	38.18
Glucose	42.24	Sucrose 5 g./100 ml.	23.55	1.26	0.948	1.000	42.22
Glucose	21.12	Sucrose 5 g./100 ml.	23.55	12.40	0.948	1.000	21.10

drops at a time at intervals of about 10~15 sec. until the end point was reached.

Operating in this way consistent results have been attained with all the reducing sugars tested, viz. glucose, lactose and galactose. On the basis of these results Table I was prepared. Over the whole of these ranges it is possible to attain a higher degree of precision, and the consistent results may be obtained, the error being within 0.06 ml., namely, 0.12 mg. in the case of glucose.

In the case of the sugar solutions containing other materials whose influence can not be overlooked, blank titration was made against the mixture of 10 ml. of the alkaline copper solution and 20 ml. of a solutions containing all materials of the same concentrations except for reducing sugars to be determined.

Some examples of glucose in solutions containing 5 and 20 g. of sucrose per 100 ml. are shown in Table II. It is important that, in all cases which have been investigated, the correction term t is not affected noticeably by contamination with other materials.

The experimental factor of the standard sugar solution should be 1.000, but a small deviation is inevitable according to the variations of the experimental conditions and personal differences in judging the end point. It is advisable to standardize the standard sugar solution, after its preparation, by titrating against a weighed pure glucose. If the deviation be large, adjustment of the standard sugar solution should be made so as to make the value of the factor approximately equal to one by adding glucose or water to the standard sugar solution.

On the other hand, it is possible to estimate the sugar content in a solution of unknown concentration. The quantity $2(B-m)tf$ gives the weight in mg. of the sugar in 20 ml. of the solution.

Some remarks should be made. Very stable and reproducible heating is possible by use of an electric heater. A reagent grade preparation of sodium hydroxide ordinally containing carbonate may be used, although the decolorization of methylene blue is somewhat slower than it is in the presence of carbonate free sodium hydroxide.

Summary

A new volumetric method determining reducing sugars has been developed by titrating a boiling mixture of modified Fehling solution and sugar solution with a standard sugar solution. By the method the concentration of sugar solution can be determined rapidly with high degree of precision.

Errors caused by variables of analytical conditions automatically being corrected, the maximum degree of accuracy will be possible by this procedure even in an unskilled hand.

There are several advantages over Lane and Eynon's method and other methods; the method is applicable over a wide range of sugar concentrations, especialy dilute solution, and in addition the difficulty in changing or washing a burette for a new solution, etc., is eliminated.

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Biochemical Studies on Pearl. VIII. Occurence of Calcite, Aragonite and Dolomite in Pearl and Shell

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Among many kinds of bivalved molluscs which are available in the pearl culture industry, *Pinctada martensii* (Dünker), the Japanese pearl oyster, is one of the most important species in Japan. In the previous papers of biochemical studies on pearl, physiological properties of the pearl oyster were reported to have a marked resemblance to the ordinary oyster[1,2] and the chemical mechanism of pearl formation was discussed from a view-point of comparative biochemisrty upon the calcification of invertebrata and vertebrata[3-5].

Several analytical results on the pearl and the shell materials of the pearl oyster have been reported[1-10], but few observations have been made on the nature of chemical constituents in the pearl and the shell.

In the present work, investigations have been made on the chemical compositions of the nacre of pearl, the nacreous portion of the shell or "mother-of-pearl", which forms an innermost layer of the shell, and the prismatic substance of an outer layer of the shell (Fig. 1). Furthermore, crystalline forms of calcium carbonate in the pearl and the shell were determined by the X-ray diffraction method. Also, a minute amount of magnesium was found in the shell and occurrence of dolomite was ascertained by a chemical method.

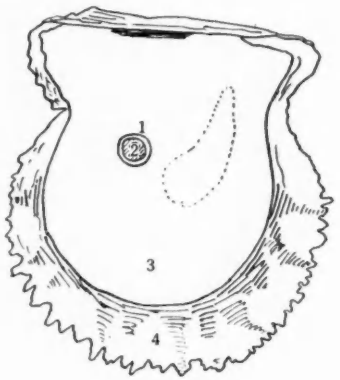

Fig. 1. A schematic diagram of the pearl and the shell of the pearl oyster.
1) The nacre of the pearl; 2) The nuclei of the pearl; 3) The nacreous layer of the shell; 4) The prismatic layer of the shell.

Experimental

Materials.—Cultured pearls used in the following experiments were collected from three-year old Japanese pearl oysters, while shell samples were obtained from pearl oysters of two winters***.

The cultured pearls were separated into nacres and nuclei mechanically, the latter being put aside. By scraping off the outer layers with a grinding-wheel, a nacreous substance of the inner layers of shells was prepared. A prismatic substance of the outer layers was obtained mechanically from thin posterior shell margins. These materials were first crushed into pieces by means of a porcelain mortar and, then, pulverized after drying at room temperature for a few days.

Calcium carbonate crystals for the X-ray diffraction analysis were prepared from the pearls and the shell substances by immersing the pulverized materials in one per cent sodium hypochlorite solutions for a few hours to remove organic substances.

Methods.—The chemical compositions of the

* A part of this study was carried out by the author, at Kobe University, Kobe.

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1) S. Tanaka and H. Hatano, *J. Chem. Soc. Japan, Pure Chem. Sec. (Nippon Kagaku Zasshi)*, **73**, 870 (1952).
2) S. Tanaka and H. Hatano, ibid., **74**, 74 (1953).
3) S. Tanaka and H. Hatano, *Publ. Seto Mar. Biol. Lab. Kyoto Univ.*, **II** (2), 341 (1952).
4) S. Tanaka and H. Hatano, *J. Chem. Soc. Japan, Pure Chem. Sec. (Nippon Kagaku Zasshi)*, **76**, 602 (1955).
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7) J. Tsutsumi, *Mem. Coll. Sci. Kyoto Univ., Ser. A*, **11**, 217, 401 (1928); **12**, 199 (1929).
8) J. Ogushi, "Studies on Pearl (Shinju no Kenkyu)", Ito Bunshindo, Tokyo (1938), p. 143.
9) K. Wada, *Bull. Natl. Pearl Res. Lab. Japan*, **1**, 1, 7 (1956); **2**, 74 (1957).
10) Y. Sawada, ibid., **2**, 68 (1957).

*** The authors wish to express their hearty thanks to Mr. K. Isowa, the president of the Nippon Pearl Co., at Matoya Bay near Kashikojima in Mie-ken for his kind presentation of these materials.

pearl and the shell materials were determined by the methods reported in the previous papers[1,2]; moisture was determined by measuring the decrease in weight on drying at 105°C for about 24 hr. until the weight came to a definite constant; total nitrogen was determined by a semi-micro-Kjeldahl's technique; total ashes were determined by igniting any sample to a constant weight at approximately 700°C and making a correction for the ignition loss of carbonate. Inorganic constituents in the ashes were determined as follows: phosphate as ammonium phosphomolybdate, calcium as calcium oxalate, sulfate as barium sulfate, and magnesium as ammonium magnesium phosphate after being separated from calcium, respectively; the carbonate content was calculated from the amount of carbon dioxide determined by the Conway's microdiffusion method[11].

Conchiolin, a screloprotein contained in the pearl and the shell, was estimated from the amount of residue remaining after the inorganic constituents were dissolved in dilute hydrochloric acid[12].

X-ray diffraction patterns of crystalline calcium carbonate in the pearl and the shell were recorded by the Norelco's X-ray diffractometer and were compared with those of the standard crystals of calcite and aragonite.

The state of chemical combination of a minute amount of magnesium which was found in the pearl as well as the shell was determined by the chemical method established by Kitano[13]. The principle of his method is as follows. When a small amount of magnesium is contained in calcareous shells, it is expected to be present in one of the only two possible forms, i.e. dolomite $CaMg(CO_3)_2$ and a solid solution of calcite and dolomite. Now, when carbon dioxide gas is passed into mixed suspensions of calcium

Table I. Amounts of calcium and magnesium dissolved into suspensions which contain magnesium compounds, under the condition of being saturated with carbon dioxide[a]

Suspension					Dissolved quantity		Ratio[e]	
$CaCO_3$[b] g.	Shell[c] g.	$CaMg(CO_3)_2$[d] g.	Ca mg.	Mg mg.	Ca mg./200 ml.	Mg	Ca %	Mg %
*1.61	—	0.89	841	117	91	1.0	10.9	0.9
*1.97	—	0.53	904	70	99	0.8	10.9	1.1
*2.06	—	0.44	920	58	91	0.5	9.9	0.8
*2.33	—	0.17	967	23	90	0.3	9.3	1.4
*2.39	—	0.11	980	14	100	0.2	10.2	1.1
**2.5	0.0	—	838	101	76	6.8	9.0	6.6
**2.0	0.5	—	870	81	71	5.7	8.2	7.0
**1.0	1.5	—	935	41	68	2.6	7.3	6.3
**0.5	2.0	—	968	20	67	2.3	6.9	12
**0.2	2.3	—	987	8.1	68	2.3	6.9	29

a) Into a suspension containing 2.5 g. of magnesium preparation in 200 ml. of distilled water, purified carbon dioxide was passed for 25 min. After being allowed to stand for 10 min., the suspension was filtered through a sheet of Toyo Roshi No. 6 filter paper. Total quantities of calcium and magnesium ions in the filtrate were determined by the volumetric method using EDTA, while the amount of calcium ion was estimated as calcium oxalate, and then the amount of magnesium ion was calculated from these two values, or was determined directly by the volumetric method using oxim reagents.

b) Extra pure reagents of calcite and aragonite prepared by Y. Kitano were used in this experiment.

c) As a standard preparation of a solid solution of calcite and aragonite, were used shells of four kinds of sea urchins, in which the magnesium had been found to be present in the form of a solid solution by X-ray diffraction techniques.

d) A dolomite preparation found at Kuzuo, Tochigi-ken, was used. The analytical results are as follows: CaO, 33.80; MgO, 19.37; clay, 0.22%.

e) [g. of Ca^{2+}(Mg^{2+}) dissolved into 200 ml. of a suspension] × 100/[g. of Ca^{2+}(Mg^{2+}) in 2.5 g. of a suspension].

* See Ref. 13.

** Y. Kitano, unpublished data (1958).

11) E.J. Conway, "Microdiffusion Analysis and Volumetric Error", Crosby Lockwood & Son, Ltd., London (1950), p. 87; E. J. Conway and A. Byrne, *Biochem. J.*, **27**, 419 (1933).

12) S. Tanaka et al., *J. Chem. Soc. Japan, Pure Chem. Sec. (Nippon Kagaku Zasshi)*, **74**, 193 (1953).

13) Y. Kitano, ibid., **77**, 211 (1956).

carbonate with dolomite or into those of calcium carbonate with a solid solution of calcite and dolomite, the quantities of magnesium dissolved into the suspensions are not the same for two cases. The data obtained by Kitano[13] are given in Table I. On the basis of these results, therefore, the state of chemical combination of magnesium present in calcareous shells can be determined by measuring the quantity of magnesium dissolved in water saturated with carbon dioxide.

Results and Discussion

Chemical Composition. — The chemical compositions of the pearl and the shell of the pearl oyster are shown in Table II, which indicates that the pearl as well as the shell contain about ninety per cent of calcium carbonate and a few per cent of conchiolin. It seems to be noticeably

TABLE II. THE CHEMICAL COMPOSITIONS OF THE NACRE OF THE PEARL AND OF THE SHELL VALVES OF THE JAPANESE PEARL OYSTER, *Pinctada martensii* (DÜNKER)*

	Cultured	Shell	
	pearl nacre %	Nacreous layer %	Prismatic layer %
Total nitrogen	0.43	0.53	1.01
Conchiolin	2.72	2.83	9.61
Pigments	±	±	+++
Reducing substance	0.00	0.00	0.02
Total ashes	80.60	89.60	76.00
Calcium	27.71	29.35	27.47
Magnesium	0.12	0.12	0.59
Carbonate	56.95	58.19	56.41
Phosphate	0.01	0.06	0.06
Sulfate	0.66	0.59	1.09

* Free from water content.

characteristic that, contrary to various calcareous tissues of vertebrata, there are little or only minute amounts of phosphate and sulfate in the pearl and the shell of the pearl oyster. Less content of conchiolin and a larger amount of calcium carbonate in the nacre than in the prismatic substance are observed. Scant amounts of pigments are present in the pearl and the nacreous oyster, while plenty of coloring substances can be found in prismatic substances[14]. Compared with the case of the nacre, relatively large amounts of magnesium are contained in the prismatic layer of the shell.

The curves shown in Fig. 2 indicate the X-ray diffraction patterns, recorded by

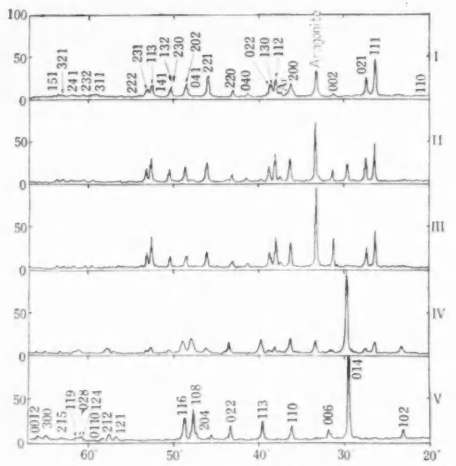

Fig. 2. X-ray diffraction patterns of calcium carbonate crystals in the nacre of pearl and in the shell material of the pearl oyster, *Pinctada martensii*. Pattern I: standard aragonite crystals; II: crystals in the nacre of the pearl; III: crystals in the nacreous layer of the shell; IV: crystals in the prismatic material; V: standard calcite crystal.

Norelco's apparatus****, of crystalline preparations of calcium carbonate from the pearl and shell materials. The crystals of calcium carbonate existing in the nacre of pearl and in the nacreous layer of shell were identified as aragonite crystals of a rhombohedral lattice, and those in the prismatic layer as calcite crystals of a rhombic lattice.

Calcite is known to form the most stable lattice of calcium carbonate while aragonite is less stable under usual crystallographical conditions. For aragonite crystal to be produced, therefore, certain special conditions should be given such as higher temperature, higher pH value of surrounding media, or a larger growing rate of crystals due to sudden supply of materials[15,16]. In connection with these requirements, it may be considered that the presence of relatively large amounts of magnesium ion is favorable to the formation of aragonite crystals.

Magnesium preparations prepared from the pearl and the shell were treated by the same procedure and the results obtained

14) Y. Takagi and S. Tanaka, ibid., **76**, 406 (1955).

**** The authors wish to express their thanks to the operating committee of this apparatus in Osaka University, for these measurements.

15) Y. Kitano and M. Nishimura, ibid., **76**, 581 (1955).

16) Y. Kitano, *J. Chem. Soc. Japan, Ind. Chem. Sec. (Kogyo Kagaku Zasshi)*, **59**, 1345 (1956).

TABLE III. RESULTS SHOWING THE OCCURRENCE OF DOLOMITE IN THE PEARL AND THE SHELL MATERIALS OF THE PEARL OYSTER*

Preparation	Suspension			Dissolved quantity		Ratio	
	Sample mg.	Ca mg.	Mg mg.	Ca mg./200 ml.	Mg	Ca %	Mg %
Pearl, nacre	952.2	240.8	1.14	20.0	0.01	8.3	0.9
Shell, nacreous substance	954.6	287.0	1.14	16.3	0.0	5.7	0
Shell, prismatic substance	973.8	267.5	5.84	14.3	1.72	5.3	29.3

* The procedure of this analysis is quite identical with that in Table I.

are presented in Table III. Comparing these results with the data in Table I, it has been determined that magnesium in the nacre of pearls and in the nacreous layer of shells exists as dolomite and that in the prismatic layer as a solid solution of calcite and dolomite.

Several experiments have been carried out on the formation of calcareous skeletons in marine organisms and it is demonstrated that the temperature is one of the most effective factors on differentiation of the composition of calciferous skeleton in some marine invertebrates[17,18]. Any other possible factors may be expected to alter the modification and the chemical composition of a crystal.

According to the experimental data in Table III, the fact that magnesium carbonate is difficult to crystallize in a rhombic lattice owing to a geometrical correlation of constituent atoms, seems to have some relations with the mode of crystallization of calcium carbonate in the pearl oyster.

Summary

The chemical compositions of the pearl and the shell of the Japanese pearl oyster were investigated from a crystallographical and biochemical point of view.

By the X-ray diffraction analysis, crystals of calcium carbonate in the nacre of pearl and in the nacreous layer of shell were determined to be aragonite, while those in the prismatic layer were shown to be calcite.

The state of chemical combination of minute amounts of magnesium present in the pearl and the shell materials was examined by a chemical method. In the nacreous substances, magnesium is present as dolomite, while in the prismatic material it exists as a solid solution of calcite and dolomite.

The state of crystals of calcium carbonate and magnesium carbonate occurring in the pearl oyster has been discussed with respect to the formation of the pearl and the shell of the pearl oyster.

The authors wish to express their gratitude to Dr. Y. Kitano, Nagoya University, Nagoya, for his kind permission to quote his unpublished data in Table I and also for his advice which was given throughout the course of this research.

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17) H. A. Lowenstam, *J. Geol.*, **62**, 284 (1954).
18) K. E. Chave, ibid., **62**, 266, 587 (1954).

Ionic Character and Hybridization in the Hydrogen Cyanide Molecule

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It is well known that the nuclear quadrupole coupling constant eQq is intimately related to the electronic structure near the nucleus of a molecule. Townes and Dailey[1] have explained especially the ionic character and the hybridization of an atom from the analysis of the experimental values of the nuclear quadrupole constants. They have considered that the existence of a field gradient q is attributable to unbalanced electrons, i.e. p or d electrons in the valence shell.

Schatz has studied the ionic character and the hybridization of chlorine in discussing the chlorine, hydrogen chloride and methyl chloride molecules[2], using the experimental values of the dipole moment besides the quadrupole coupling constant, and has stressed the importance of including the overlap integral for the estimation of the quadrupole coupling constant. However, his calculations of the field gradient are essentially based on the theory by Townes and Dailey[1]. Namely, he assumed the total quadrupole coupling constant dependent upon only the $3p$ and $3d$ electrons of chlorine and ignored the effects of other electrons and nuclei in the molecule.

In this paper, the ionic character and the s character of the nitrogen atom in a hydrogen cyanide molecule have been investigated by means of the theoretical evaluation of the dipole moment and the quadrupole coupling constant taking into account the effects of all the electrons and nuclei in a hydrogen cyanide molecule.

Calculation Method

Basic Wave Function. — The hydrogen cyanide molecule is a linear molecule having an NC bond distance equal to 1.156 Å and a CH bond distance equal to 1.1064 Å as determined by microwave measurements[3]. The hydrogen cyanide molecule is taken to lie along the Z axis with its nitrogen atom at the origin. The total wave function used is the following valence bond function including an ionic term ($N^-\equiv C^+$), that is,

$$\Psi_T = A\left[\Psi_{cov} + \lambda_1\Psi_{\sigma ion} + \lambda_2(\Psi_{\pi_x ion} + \Psi_{\pi_y ion})\right] \quad (1)$$

Where A is the normalization factor and four state functions appearing in Eq. 1 are taken as simple products of the following electron pair bond functions with the Heitler-London type:

$$\begin{aligned}
\Psi_{cov} &= (NC:\sigma)^2(CH:\sigma)^2(N_2:\sigma)^2 \\
&\quad\times(NC:\pi_x)^2(NC:\pi_y)^2 \\
\Psi_{\sigma ion} &= (N_1:\sigma)^2(CH:\sigma)^2(N_2:\sigma)^2 \\
&\quad\times(NC:\pi_x)^2(NC:\pi_y)^2 \\
\Psi_{\pi_x ion} &= (NC:\sigma)^2(CH:\sigma)^2(N_2:\sigma)^2 \\
&\quad\times(N:\pi_x)^2(NC:\pi_y)^2 \\
\Psi_{\pi_y ion} &= (NC:\sigma)^2(CH:\sigma)^2(N_2:\sigma)^2 \\
&\quad\times(NC:\pi_x)^2(N:\pi_y)^2
\end{aligned} \quad (2)$$

and

$$\begin{aligned}
(NC:\sigma)^2 &= A_1[n_1(i)c_2(j) + c_2(i)n_1(j)] \\
(CH:\sigma)^2 &= A_2[c_1(i)h(j) + h(i)c_1(j)] \\
(NC:\pi_x)^2 &= A_3[n_{\pi_x}(i)c_{\pi_x}(j) \\
&\quad + c_{\pi_x}(i)n_{\pi_x}(j)] \\
(N:\pi_x)^2 &= n_{\pi_x}(i)n_{\pi_x}(j) \\
(N_1:\sigma)^2 &= n_1(i)n_1(j)
\end{aligned} \quad (3)$$

$(NC:\pi_y)^2$, $(N:\pi_y)^2$ and $(N_2:\sigma)^2$ are taken with the analogous definitions to $(NC:\pi_x)^2$, $(N:\pi_x)^2$ and $(N_1:\sigma)^2$, respectively. Therefore, in the wave function used, the higher order permutation of the electrons is neglected; that is, the orthogonarity among the electron pair bonds is assumed. The coefficients A_1, A_2 and A_3 of the electron pair bond functions are easily shown to be

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1) C. H. Townes and B. P. Dailey, *J. Chem. Phys.*, **17**, 782 (1949).

2) P. N. Schatz, ibid., **22**, 695 (1954); **22**, 755 (1954); **22**, 1974 (1954).

3) J. W. Simmon, W. E. Anderson and W. Gordy, *Phys. Rev.*, **77**, 77 (1950).

$$
\begin{aligned}
A_1 &= [2(1+S_{n_1c_2}^2)]^{-1/2} \\
A_2 &= [2(1+S_{c_1h}^2)]^{-1/2} \\
A_3 &= [2(1+S_{n_\pi c_\pi}^2)]^{-1/2} \\
S_{n_1c_2} &= \int n_1 c_2 \mathrm{d}v \qquad S_{c_1h} = \int c_1 h \mathrm{d}v \\
S_{n_\pi c_\pi} &= \int n_\pi c_\pi \mathrm{d}v
\end{aligned} \tag{4}
$$

Futhermore h, $c_{\pi x}$, $c_{\pi y}$, $n_{\pi x}$ and $n_{\pi y}$ are atomic orbitals (AO), and n_1, n_2, c_1 and c_2 are the following $s-p$ hybridized orbitals:

$$
\begin{aligned}
n_1 &= \alpha^{1/2}(N:2s) + (1-\alpha)^{1/2}(N:2pz) \\
n_2 &= (1-\alpha)^{1/2}(N:2s) - \alpha^{1/2}(N:2pz) \\
c_1 &= 2^{-1/2}[(C:2s) + (C:2pz)] \\
c_2 &= 2^{-1/2}[(C:2s) - (C:2pz)]
\end{aligned} \tag{5}
$$

All the AO's except the $2p$ orbitals of nitrogen are the Slater orbitals[4] (assumed effective nuclear charge $\delta_h=1.17$, $\delta_c=1.625$ and $\delta_n=1.95$). The $2p$ orbitals of nitrogen have a great effect on the field gradient at the nitrogen nucleus. Then, the following analytic function derived from the Hartree-Fock field calculation of the ground state ^4S of the nitrogen atom[5] is used for its radial function instead of the Slater orbital,

$$
\begin{aligned}
R_{2p} = r[&1.809\exp(-1.387r) \\
&+6.620\exp(-2.950r)]
\end{aligned} \tag{6}
$$

Dipole Moment.—The experimental value of the dipole moment of hydrogen cyanide has been known to be 3.00 D[3] and also it is given by the expression

$$
\mu_T = e\left(\sum_{i=1}^{2} r_i - \sum_{j=1}^{10} \overline{Z}_j\right) \tag{7}
$$

$$
\sum_{i=1}^{2} r_i = 6.7440\ \text{Å} \qquad \overline{Z}_j = \int |\Psi_T|^2 Z_j \mathrm{d}v \tag{8}
$$

Where e is the protonic charge (4.80288×10^{-10} esu), the first and the second term in Eq. 7 are, respectively, the contributions of the nuclei and the electrons. When the latter are calculated by the wave function given in Eq. 1, the expression is easily shown to be

$$
\sum_{j=1}^{10} Z_j = M_{cov} + M_{\sigma ion} + M_{\pi ion} + M_{trans} \tag{9}
$$

where

$$
\begin{aligned}
M_{cov} &= 2[M(NC:\sigma) + M(CH:\sigma) \\
&\quad + 2M(NC:\pi) + M_{n_2n_2}] \\
M_{\sigma ion} &= 2\lambda_1^2[M(CH:\sigma) + 2M(NC:\pi)] \\
M_{\pi ion} &= 4\lambda_2^2[M(NC:\sigma) + M(CH:\sigma) \\
&\quad + M(NC:\pi) + M_{n_2n_2}] \\
M_{trans} &= 4\lambda_1 A_1[M_{n_1c_2} + 2S_{n_1c_2}\{M(CH:\sigma) \\
&\quad + 2M(NC:\pi) + 1/2M_{n_2n_2}\}] \\
&\quad + 8\lambda_2 A_3[M_{n_\pi c_\pi} + 2S_{n_\pi c_\pi}\{M(NC:\sigma) \\
&\quad + M(CH:\sigma) + M(NC:\pi) + M_{n_2n_2}\}] \\
&\quad + 16\lambda_1\lambda_2 A_1 A_3[S_{n_\pi c_\pi} M_{n_1c_2} \\
&\quad + S_{n_1c_2} M_{n_\pi c_\pi} + 2S_{n_1c_2} S_{n_\pi c_\pi} \\
&\quad \times\{M(CH:\sigma) + M(NC:\pi) \\
&\quad + 1/2M_{n_2n_2}\}]
\end{aligned} \tag{10}
$$

and the following abbreviations are adopted:

$$
\begin{aligned}
M(NC:\sigma) &= A_1^2(M_{n_1n_1} + M_{c_2c_2} \\
&\quad + 2S_{n_1c_2}M_{n_1c_2}) \\
M(CH:\sigma) &= A_2^2(M_{c_1c_1} + M_{hh} \\
&\quad + 2S_{c_1h}M_{c_1h}) \\
M(NC:\pi) &= A_3^2(M_{c_\pi c_\pi} + 2S_{n_\pi c_\pi}M_{n_\pi c_\pi})
\end{aligned} \tag{11}
$$

Also the normalization factor A is shown to be

$$
\begin{aligned}
A = (&1+\lambda_1^2+2\lambda_2^2+4A_1S_{n_1c_2}\lambda_1+8A_3S_{n_\pi c_\pi}\lambda_2 \\
&+16A_1A_3S_{n_1c_2}S_{n_\pi c_\pi}\lambda_1\lambda_2)^{-1/2}
\end{aligned} \tag{12}
$$

The necessary integrals of the dipole moment matrices: $M_{ab} = \int \chi_a Z \chi_b \mathrm{d}v$ and the overlap integrals: $S_{ab} = \int \chi_a \chi_b \mathrm{d}v$ are given to Table I. These values are obtained by the ordinary method[6].

Quadrupole Coupling Constant.—The experimental value of the nuclear quadrupole coupling constant has been known from the microwave datum to be -4.58 Mc.[3] On the other hand, the quadrupole coupling constant is shown to have the following expression:

$$
eQq_T = eQ(q_n + q_{el}) \tag{13}
$$

$$
q_n = 0.79295e \ e\ \text{a.u.}
$$

$$
q_{el} = -e\int |\Psi_T|^2 (3\cos^2\theta_z - 1)\, r^{-3} \mathrm{d}v \tag{14}
$$

Where q_T is the average value of $(\partial^2 V/\partial Z^2)_{z=0}$, V being all the electrostatic potentials and Q the nuclear quadrupole moment of nitrogen ($=2\times10^{-26}$ cm^2)[1]. In Eq. 13, the

4) J. C. Slater, ibid., **36**, 57 (1932).
5) D. R. Hartree and W. Hartree, *Proc. Roy. Soc. (London)*, **A193**, 299 (1948).
6) For example, M. Kotani et al., "Table of Molecular Integrals", Maruzen Co., Ltd., Tokyo (1955).

TABLE I. VALUES OF MOLECULAR INTEGRALS:

$$S_{ab}=\int\chi_a\chi_b d\nu,\quad M_{ab}=\int\chi_a Z\chi_b d\nu$$

(in Angstrom as unit)

S_{c_sh}	0.50876	M_{c_sh}	0.012501
$S_{c_\sigma h}$	0.49357	$M_{c_\sigma h}$	0.16891
$S_{n_sc_s}$	0.47011	$M_{n_sc_s}$	−0.040613
$S_{n_sc_\sigma}$	−0.49979	$M_{n_sc_\sigma}$	0.18131
$S_{n_\sigma c_s}$	0.39765	$M_{n_\sigma c_s}$	0.13353
$S_{n_\sigma c_\sigma}$	−0.30254	$M_{n_\sigma c_\sigma}$	−0.026792
$S_{n_\pi c_\pi}$	0.29880	$M_{n_\pi c_\pi}$	−0.020225
		$M_{c_sc_\sigma}$	0.47003
		$M_{n_\sigma n_s}$	0.39169

The following abbreviated notations for AO's are used; $h=(H{:}1s)$, $c_s=(C{:}2s)$, $c_\sigma=(C{:}2pz)$, $c_\pi=(C{:}2px$ or $2py)$, $n_s=(N{:}2s)$, $n_\sigma=(N{:}2pz)$ and $n_\pi=(N{:}2px$ or $2py)$. The one-center and the two-center integrals are respectively evaluated with the nucleus in question and the center of internuclear distance as the origin.

first and the second term on the right are, respectively, the contributions of the nuclei except the nitrogen nucleus and the electrons to the field gradient q_T. q_{el} is calculated by Eq. 1 as follows:

$$\begin{aligned}q_{el}=&-2[q(NC:\sigma)+q(CH:\sigma)\\&+2q(NC:\pi)+q_{n_2n_2}]\\&+2\lambda_1^2[q(CH:\sigma)+2q(NC:\pi)+2q_{n_1n_1}]\\&+4\lambda_2^2[q(NC:\sigma)+q(CH:\sigma)+q(NC:\pi)\\&+q_{n_2n_2}+q_{n_\pi n_\pi}]\\&+4A_1\lambda_1[q_{n_1c_2}+2S_{n_1c_2}\{q(CH:\sigma)\\&+2q_{n_\pi c_\pi}+3/2\,q_{n_1n_1}\}]\\&+8A_3\lambda_2[q_{n_\pi c_\pi}+2S_{n_\pi c_\pi}\{q(NC:\sigma)\\&+q(CH:\sigma)+q_{n_2n_2}+q_{n_\pi c_\pi}+1/2\,q_{n_\pi n_\pi}\}]\\&+16A_1A_3\lambda_1\lambda_2[S_{n_\pi c_\pi}q_{n_1c_2}+S_{n_1c_2}q_{n_\pi c_\pi}\\&+2S_{n_1c_2}S_{n_\pi c_\pi}\{q(CH:\sigma)\\&+q(NC:\pi)+3/2\,q_{n_1n_1}+1/2\,q_{n_\pi n_\pi}\}]\end{aligned}\qquad(15)$$

Here the following abbreviations are adopted:

$$\left.\begin{aligned}q(NC:\sigma)&=A_1^2(q_{n_1n_1}+q_{c_2c_2}\\&\quad+2S_{n_1c_2}q_{n_1c_1})\\q(CH:\sigma)&=A_2^2(q_{c_1c_1}+q_{hh}+2S_{c_1h}q_{c_1h})\\q(NC:\pi)&=A_3^2(q_{n_\pi n_\pi}+q_{c_\pi c_\pi}\\&\quad+2S_{n_\pi c_\pi}q_{n_\pi c_\pi})\end{aligned}\right\}\qquad(16)$$

All $q_{ab}=-eq_{ab}'=-e\int\chi_a(3\cos^2\theta_z-1)/r^3\chi_b d\nu$ are calculated by using the methods of Barnett and Coulson[7]. These values are given in Table II.

TABLE II. VALUES OF FIELD GRADIENT INTEGRALS:

$$q_{ab}'=\int\chi_a(3\cos^2\theta_z-1)/r^3\chi_b d\nu\ \text{(in atomic unit)}$$

$q_{n_\sigma n_\sigma}'$	2.36606	$q_{c_sc_s}'$	0.098460
$q_{n_\pi n_\pi}'$	−1.18303	$q_{c_sc_\sigma}'$	−0.048937
$q_{n_sc_s}'$	0.030116	$q_{c_\sigma c_\sigma}'$	0.133908
$q_{n_sc_\sigma}'$	−0.045963	$q_{c_\pi c_\pi}'$	0.080736
$q_{n_\sigma c_s}'$	0.102260	q_{hh}'	0.011326
$q_{n_\sigma c_\sigma}'$	−0.160130	q_{c_sh}'	0.027928
$q_{n_\pi c_\pi}'$	−0.012108	$q_{c_\sigma h}'$	0.035842

The three-center integrals q_{c_sh}' and $q_{c_\sigma h}'$ are evaluated by Ruedenberg-Mulliken's approximation[8]:

$$\int\chi_a 1/r_c^3\chi_b d\nu\approx 1/2\,S_{ab}\left(\int|\chi_a|^2 1/r_c^3 d\nu+\int|\chi_b|^2 1/r_c^3 d\nu\right)$$

Results and Discussion

The parameters to be determined are the ionic characters λ_1, λ_2 and the $s-p$ hybridization of nitrogen α. Now, in use of Eqs. 7 and 13, the relation of λ_1 and λ_2

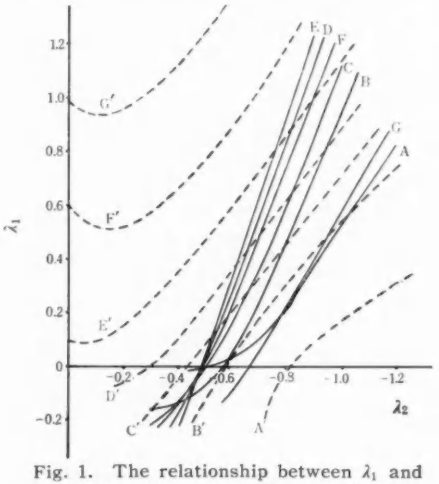

Fig. 1. The relationship between λ_1 and λ_2, being chosen in all cases to give the experimental values. α is taken as a parameter. The full and dotted lines are respectively the curves of the dipole moment and the quadrupole coupling constant.

A:	$\alpha=0.2$	A':	$\alpha=0.20$
B:	$\alpha=0.3$	B':	$\alpha=0.30$
C:	$\alpha=0.4$	C':	$\alpha=0.35$
D:	$\alpha=0.5$	D':	$\alpha=0.40$
E:	$\alpha=0.6$	E':	$\alpha=0.45$
F:	$\alpha=0.7$	F':	$\alpha=0.50$
G:	$\alpha=0.8$	G':	$\alpha=0.60$

7) M. P. Barnett and C. A. Coulson, *Trans. Roy. Soc. (London)*, **243**, 221 (1951).

8) R. S. Mulliken, *J. chim. phys.*, **46**, 497 (1949); K. Ruedenberg, *J. Chem. Phys.*, **19**, 1433 (1951).

which are taken to coincide with the experimental values is shown in Fig. 1, in which the hybridization α is taken as a parameter. From Fig. 1, it is seen that the dipole moment is not much affected by the *s* character between $\alpha=0.3$ and 0.7, but it depends on the ionicity as a considerable extent. This will explain the well-known fact that there is a possibility to take up the ionic character as a measure of the dipole moment[9]. On the other hand, the eQq curves are intensely dependent upon the *s* character, too. The α, λ_1 and λ_2 values are not determined simultaneously, but it will be clear from Fig. 1 that the region of allowed α value is between about 0.3 and 0.5. Now, it is possible to calculate the NC bond moment under the same scheme as above. The NC bond moments for the reasonable set of α, λ_1 and λ_2 obtained from Fig. 1 are as follows:

α	λ_1	λ_2	NC bond moment
0.50	1.81	−1.16	2.57 D
0.45	1.04	−0.94	3.38 D
0.40	0.61	−0.80	1.61 D
0.35	0.35	−0.72	1.59 D
0.30	0.04	−0.60	1.42 D

The NC bond moment has been estimated to be about 3.5 D by Smyth[10]. If his estimation is correct, a reasonable set of three parameters would be taken to be $\alpha=0.45$, $\lambda_1=1.04$ and $\lambda_2=-0.94$. Then, the experimental value of total molecular dipole moment of the hydrogen cyanide molecule 3.0 D can be explained to be 3.4 D (N^-C^+ bond moment) plus −0.4 D (C^+H^- bond moment). The value −0.4 D for the C^+H^- bond moment may be acceptable taking into account the inclusion of the atomic dipole term by Coulson[11].

From the eQq data, Townes and Dailey[1] and separately Dailey[12] have estimated the structure of HCN as follows:

Structure		Assumed *s* character	Assumed eQq per *p* electron**	
Covalent	Ionic			
90%	10%	25%	−24 Mc.	Townes &
or 90%	10%	50%	−10 Mc.	Dailey
90%	10%	45%	—	Dailey

In both estimates, obviously some arbitrariness exists in the determination of the parameters because of several having been obtained from only one experiment value. On the other hand, Pauling[13] has presumed that the ionicity of the NC bond would probably have about 57% from the experimental values of the dipole moment of alkyl cyanides. The relative weights of structures are expressed in the following two ways; the one is due to the definition that the weights of the covalent and two ionic parts are given in the ratio $1:\lambda_1^2:2\lambda_2^2$ by Coulson[14] (I), and the other includes a transitional structure as well as covalent and ionic by Syrkin and Dyatkina[15] (II). Then, the following results are obtained from the present calculation:

Structure		Weight of structure, % By I	By II
Covalent	(A)	26.0	10.2
σ ionic	(B)	28.1	11.2
π_x & π_y ionic	(C)	45.9	18.1
Transitional	(A)—(B)		21.3
〃	(A)—(C)		19.3
〃	(B)—(C)		20.0

Following the definition by Coulson, the present result with 74% as the ionic structure seems rather to support Pauling's conclusion. Here it is interesting to note that in a triple bond NC, each structure with the σ or π polarized bond has nearly equal weight, notwithstanding the fact that σ bond has larger overlap (~0.7) and, on the other hand, π bond smaller overlap (~0.3). However, it is probably impossible in the present calculation to state anything about the relationship between the degree of the overlap of each bond in the multiple bond and the polarization of the bond or the mobilities of electron in bond.

Fig. 2 shows the curves of the quadrupole coupling constants calculated, taking into account only *p* electrons of nitrogen and all the charges for the field gradient at the nitrogen nucleus with $\alpha=0.45$. Now, being taken to fix λ_1 and λ_2 values, the eQq values taking into account the contribution of all the charges are always larger than ones for only *p* electrons. This difference probably depends upon whether or not the charge distribution in the overlap

9) L. Pauling, "The Nature of the Chemical Bond", Cornell Univ. Press, Ithaca, N. Y. (1940), p. 46.
10) C. P. Smyth, *J. Am. Chem. Soc.*, **60**, 183 (1938).
11) C. A. Coulson, *Trans. Faraday Soc.*, **38**, 433 (1942).
12) B. P. Dailey, *J. Phys. Chem.*, **57**, 490 (1953).
** Using Eq. 6, the authors obtain −11.12 Mc. for eQq per $2pz$ electron; Y. Kato et al., This Bulletin, **32**, 527 (1959).
13) See Ref. 9, p. 75.
14) C. A. Coulson, "Valence", Oxford Univ. Press, London (1952), p. 123.
15) Y. K. Syrkin and M. E. Dyatkina, "Structure of Molecules and the Chemical Bond", Butterworths Scientific Publications, London (1950), p. 205.

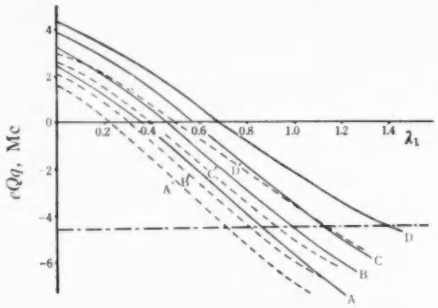

Fig. 2. Quadrupole coupling constant of HCN as a function of λ_1. λ_2 is taken as a parameter and α is fixed to 0.45. The horizontal chain line is the experimental value. The full and dotted lines are respectively the curves under the consideration of all the charge and only p electrons for the field gradient at the nitrogen nucleus.

A & A': $\lambda_2 = -0.8$
B & B': $\lambda_2 = -0.9$
C & C': $\lambda_2 = -1.0$
D & D': $\lambda_2 = -1.1$

region is taken into account in evaluating the field gradient. Gordy[16] has argued that the overlap effects should be ignored and has pointed out the merits of his simple relation between the ionicity and quadrupole coupling constant in which the s character is neglected entirely. Certainly the field gradient is proportional to $1/r^3$, but at the same time to the charge density. Therefore, it should be naturally required for the evaluation of the nuclear quadrupole coupling constant to take into account not only the redistribution of the charge near the nucleus due to the formation of the chemical bond, but also the distribution of the charge in bonding region because of its larger density.

In this point, the present results will support Schatz's calculation of eQq including the overlap effects.

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16) W. Gordy, *J. Chem. Phys.*, **19**, 792 (1951); W. Gordy, W. V. Smith and R. F. Trambarulo, "Microwave Spectroscopy", John Wiley & Sons, Inc., New York (1953), p. 272.

Spectrophotometric Determination of Nitrous Acid with Disodium 1-(4'-Aminobenzeneazo)-amino-8-hydroxy-naphthalene-2', 6-disulfonate

By Yukiteru KATSUBE and John H. YOE

(Received July 27, 1959)

Colorimetric methods in general use for a small quantity of nitrous acid are based on the formation of intensely colored azo dyes. Nitrous acid reacts with primary aromatic amines in acid solution to form diazonium salts, which react with a second molecule of the amine to produce colored cations of an aminoazo compound. Although the intense color of the azo dyestuffs formed in this way is available for the determination of nitrous acid, the coupling reagent used has an important influence on the determination.

The best amine that has been used for the determination of nitrous acid is sulfanilic acid (p-anilinesulfonic acid), with subsequent coupling of the resulting diazonium compound with α-naphthylamine to give the red dyestuff p-benzene sulfonic acid-azo-α-naphthylamine[1-6].

1) P. Griess, *Ber.*, **12**, 427 (1879).
2) F. L. Hahn and G. Jaeger, ibid., **58**, 2335 (1925).
3) J. Blom, ibid., **59**, 121 (1926).
4) F. P. Treadwell, "Analytical Chemistry", English Ed., Vol. II, John Wiley & Sons, Inc., New York (1951), p. 306.
5) F. Feigl, "Spot Tests", English Ed., Vol. I, Elsevier Publishing Co., New York (1954), p. 302.
6) N. A. Tananaeff and A. M. Schapowalenko, *Z. anal. Chem.*, **100**, 350 (1935).

This paper describes a new method for the determination of trace quantities of nitrous acid based on the formation of a colored compound with disodium 1-(4'-aminobenzeneazo)-2-amino-8-hydroxy-naphthalene-2',6-disulfonate.

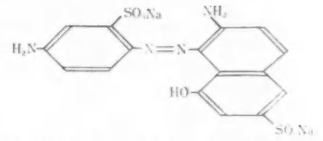


Fig. 1. Disodium 1-(4'-aminobenzeneazo)-2-amino-8-hydroxy-naphthalene-2',6-disulfonate.

Experimental

Apparatus and Reagents. — *Spectrophotometer.* — A Shimazdu Spectrophotometer with matched 1 cm. glass cells, was used.

Standard solution of nitrous acid. — The standard solution of nitrous acid was prepared according to Treadwell[4]. His instructions are as follows. Add silver nitrate to a concentrated solution of commercial potassium nitrite, filter off the precipitated silver nitrite and wash it several times with cold distilled water. To obtain pure silver nitrite, dissolve the precipitate in as little distilled water as possible and cool quickly. Drain off the mother liquor through a funnel provided with a platinum cone using gentle suction. Wash the silver nitrite on the funnel with a small volume of cold distilled water. Place the washed silver nitrite in a calcium chloride desiccator and allow to dry in the dark. Dissolve 1.5388 g. of the dried silver nitrite in a liter volumetric flask with hot distilled water and add 0.8 g. of pure sodium chloride to convert the silver nitrite into silver chloride and sodium nitrite. After cooling, make the solution up to volume with distilled water and allow the precipitate to settle. Pipet 10 ml. of the clear solution into a second liter-volumetric flask, make up to the mark with distilled water and thoroughly mix. One milliliter of this solution contains 4.7 mg. of nitrous acid.

Reagent solution. — Prepare the reagent solution by dissolving disodium 1-(4'-aminobenzencazo)-2-amino-8-hydroxy-naphthalene-2',6-disulfonate in distilled water to give a 0.05% solution. (The reagent may be obtained from the LaMotte Chemical Products Co., Chestertown, Maryland, U. S. A.)

0.4% Ethylenediaminetetraacetic acid (disodium salt) solution.

6 N Hydrochloric acid.

Procedure. — Transfer 20 ml. of EDTA solution to a 25 ml. volumetric flask and add 1 ml. of the sample solution, which has been adjusted so as to contain 5 to 60 p. p. m. of nitrous acid. Add 2.5 ml. of the reagent solution, and 0.3 ml. of 6 N hydrochloric acid and shake well. Make up to the mark with distilled water, thoroughly mix and, after ten minutes, measure the absorbance at 625 mμ, using a reagent blank solution as a reference. Determine the weight or the concentration of nitrous acid in the sample from a calibration curve.

Results and Discussion

Absorption Spectra. — Disodium 1-(4'-aminobenzeneazo)-2-amino-8-hydroxy-naphthalene-2',6-disulfonate is a red-brown solid, soluble in water. It is stable indefinitely in the solid state, and for, at least, three months when dissolved in water. The aqueous solution of the reagent is red; the nitrite ion in hydrochloric acid reacts with it to give a blue solution. Absorption spectra of the reagent solution and of the blue solution produced by the color reaction between the reagent and nitrite in diluted hydrochloric acid solution are given in Fig. 2.

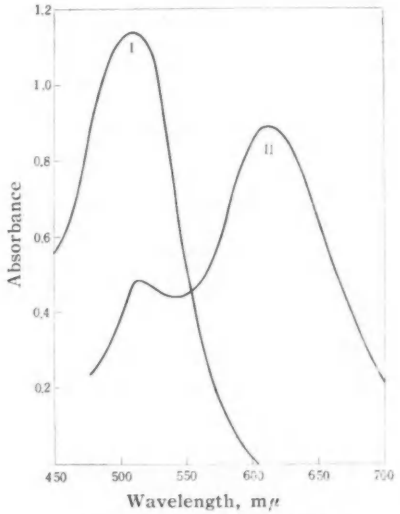


Fig. 2. Absorption spectra.
I. Reagent, 50 p. p. m.
II. Reagent (50 p. p. m.) + HNO_2 (2.3 p. p. m.)

As seen in Fig. 2, the compound produced by the color reaction has a maximum absorption at 625 mμ; the reagent solution does not absorb light at this wavelength. Hence, for analytical use absorbance measurements are made at 625 mμ. A large exess of the reagent must be avoided because its solution has a slight absorption at 625 mμ when the reagent concentration is greater than 50 p. p. m. It is not necessary to use exactly the same concentration of the reagent for standards and unknowns so far as the concentration of

unreacted reagent is below 50 p. p. m. and water is used as reference solution. However, color intensities measured with the reagent solution as a blank obey Beer's law better than those with a water blank.

Application of the method of continuous variations[7,8] to this color reaction indicates that the mole ratio of reagent to NO_2^- is 1 to 1. The result is shown in Fig. 3.

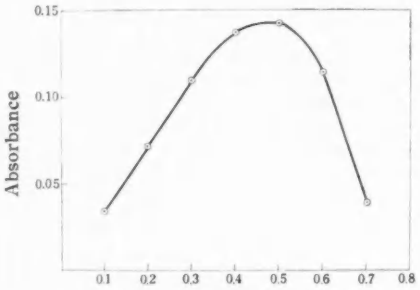


Fig. 3. Application of method of continuous variations: The nitrite and the reagent solutions were mixed in proportion to give the x to $(1-x)$ ratio of component in 1.0 ml. total volume in a 100 ml. volumetric flask, where x is equivalent to ml. of 10^{-3} M reagent and $(1-x)$ is equivalent to ml. of 10^{-3} M nitrite ion (the concentration of hydrochloric acid in the mixed solution was adjusted to 0.1 N).

Effect of Concentration of Hydrochloric Acid. — In order to determine the effect of the concentration of hydrochloric acid on the color reaction, the blue colored solution containing 2.8 p. p. m. of nitrous acid and 50 p.p.m. of the reagent were prepared with hydrochloric acid of various strengths, and absorbances of these solutions were measured. The results are shown in Fig. 4.

It is seen that the optimum concentration of hydrochloric acid is between 0.05 and 0.1 N and hence, the solution containing nitrite must be adjusted to within this concentration range. Additional acid decreases the color intensity, causing rapid decolorization. With less acid, the color does not attain a maximum intensity within a reasonable time. In the optimum acid concentration, the color increases during the first ten minutes after the preparation of the blue solution, and then remains constant for about thirty minutes. It is necessary, therefore, to allow the solution to stand ten minutes and then to measure the absorbance within thirty minutes.

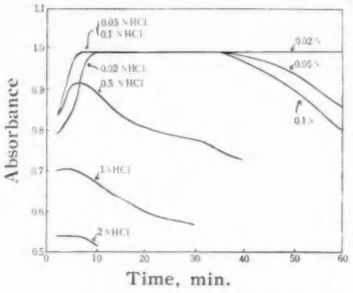


Fig. 4. Effect of hydrochloric acid.

When sulfuric, phosphoric and acetic acid are used in place of hydrochloric acid, a less intense color is obtained.

Effect of Temperature. — There is no variation in the absorbance of the color system over a temperature range of 15 to 30°C. Hence, normal temperature changes in the laboratory introduce no error.

Interfering Ions. — The reagent was tested with 67 ions on a spot plate to determine the effect of other ions. The tested ions are given in Table I as the periodic table style.

Sixteen ions shown by italics in Table I were found to cause interference (As^{+3},

TABLE I. EFFECT OF OTHER IONS

Li^+	Be^{+2}											$B_4O_7^{-2}$	CO_3^{-2}	NO_3^-	F^-
Na^+	Mg^{+2}											Al^{+3}	SiO_3^{-2}	HPO_4^{-2} S^{-2}	Cl^-
K^+	Ca^{+2}	Sc^{+3}	*Ti^{+4}*	Cr^{+3}	*Mn^{+2}* *MnO_4^-*	*Fe^{+3}* Fe^{+2}	Co^{+2}	Ni^{+2}	Cu^{+2}	Zn^{+2}		Ga^{+3}	Ge^{+4}	*As^{+3}*	*CeO_3^{-2}* *Br^-*
Rb^+	Sr^{+2}	Y^{+3}	*Zr^{+4}*	*MoO_4^{-2}*		Ru^{+3}	Rh^{+3}			Cd^{+2}		In^{+3}	*$Sn^{+2\,+4}$*	Sb^{+3}	*I^-*
Cs^+	Ba^{+2}		Hf^{+4}	UO_2^{+2}	ReO_4^-	OsO_5^{-2}	Ir^{+4}			*$Hg^{+\,+2}$*		Tl^{+3}	Pb^{+2}	Bi^{+3}	
*La^{+3}	*Ce^{+3}*	Pr^{+3}	Nd^{+3}	Sm^{+3}	Eu^{+3}			Dy^{+3}		Er^{+3}		Tm^{+3}	Yb^{+3}		

7) P. Job, *Ann. chim.*, (10), **9**, 113 (1928).

8) W. C. Vosburgh and G. R. Cooper, *J. Am. Chem. Soc.*, **63**, 437 (1941).

Br^-, Fe^{+3}, Ce^{+3}, CeO_3^{-2}, F^-, $Hg^{+,2+}$, I^-, Mn^{+2}, MnO_4^-, MoO_4^{-2}, $Sn^{+2,+4}$, Ti^{+4}, Zr^{+4}). Ferric ions cause a serious error and must be removed before the addition of the reagent. Chemical methods of separation of ferric ions did not yield good results. However, when EDTA solution is added to the sample solution before the addition of the reagent, interference of ferric ions is effectively eliminated. EDTA has no influence on the absorption spectrum of the blue colored solution. The effect of some common ions was tested spectrophotometrically; Table II summerizes the tolerance.

In Table II, the limiting concentration of an ion is taken to be the concentration that causes a deviation of more than 0.01 unit in the absorbance of a solution containing 0.94 p. p. m. of nitrous acid.

Table II. Interferences

Ion	Added as	Limiting concn., p. p. m.
Co^{+2}	$CoCl_2$	300
Cr^{+3}	$Cr_2(SO_4)_3$	200
Cu^{+2}	$CuSO_4$	300
Fe^{+3}	$Fe_2(SO_4)_3$	100
Ni^{+2}	$NiSO_4$	300

Table III. Accuracy and precision of the method

Nitrous acid		Absorbance** at 625 mμ	Standard deviation*** in absorbance unit	Error
Taken p. p. m.	Found* p. p. m.			%
0.19	0.18	0.075	0.002	−5.3
0.38	0.37	0.151	0.001	−2.6
0.56	0.57	0.231	0.001	+1.8
0.75	0.76	0.307	0.002	+1.3
0.94	0.95	0.386	0.001	+1.1
1.13	1.14	0.463	0.002	+1.0
1.31	1.31	0.534	0.003	0.0
1.50	1.51	0.611	0.002	+0.7
1.69	1.65	0.669	0.003	−2.4
1.88	1.85	0.749	0.004	−1.6
2.07		0.807	0.002	
2.26		0.864	0.002	
2.63		0.95	0.010	
2.82		0.99	0.013	
3.38		0.15	0.018	

* These values were calculated by use of 0.405 of average value, from 0.19 to 1.88 p. p. m. HNO_2, of absorbances calculated per one p. p. m. HNO_2.

** These values are the averages of six replicate determinations.

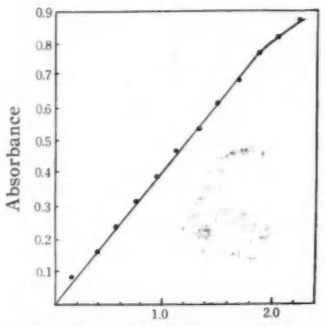
*** The standard deviations were calculated by the equation, $\sigma = \sqrt{\sum d^2/(n-1)}$, d being the deviation of each absorbance measured from the average and n the number of measurements.

Calibration Curve and Precision. — In order to construct a calibration curve and to determine the precision of the method, fifteen series of six replicate determinations were made. The precision, expressed as the standard deviation from the mean for each of the fifteen series, is shown in Table III.

The spectrophotometric sensitivity of the color reaction is 0.004 γ of nitrous acid per sq. cm. A more practical sensitivity may be taken as one part of nitrous acid in 10,000,000 parts of solution. A solution containing this concentration has an absorbance of 0.040 unit.

Beer's Law. — Beer's law is obeyed up to about 2 p. p. m. of nitrous acid and the absorbances are sufficiently reproducible to allow the range of the determination to be extended to about 3 p. p. m. (see Fig. 5).

Determination of Nitrous Acid in Synthetic Solutions Containing Various Ions. — The determination of nitrous acid in the presence of certain other ions has made. The results are given in Table IV.



Concentration of nitrous acid, p. p. m.

Fig. 5. Beer's law plot.

Table IV. Determination of nitrous acid

Solutions added	Analyzed p. p. m.	Found HNO_2 p. p. m.	Error %
1) Fe^{+3}	200		
HNO_2	0.20	0.21	+5.0
2) Fe^{+2}	400		
Fe^{+3}	400		
Cu^{+2}	200		
HNO_2	0.60	0.62	+3.3
3) Cu^{+2}	200		
Ni^{+2}	200		
Fe^{+3}	500		
HNO_2	1.80	1.78	−1.1
4) Fe^{+2}	200		
Fe^{+3}	200		
Ca^{+2}	600		
Mg^{+2}	600		
HNO_2	0.20	0.20	0.0

Summary

A procedure has been developed for the spectrophotometric determination of trace amounts of nitrous acid with disodium 1-(4'-aminobenzeneazo)-2-amino-8-hydroxynaphthalene-2',6-disulfonate. The method is accurate and precise and has a sensitivity of 0.004 γ of nitrous acid per sq. cm. Beer's law is obeyed up to about 2 p. p. m. of nitrous acid. A study of the effect of many ions on the color reaction has been made. The interference of ferric ions is eliminated by the use of EDTA.

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Estimation of the Energy of Hydrogen Bonds Formed in Crystals. II. Phenols

By Ariyuki AIHARA

(Received July 20, 1959)

The OH···O bonding is the most familiar of the hydrogen bonds and has already been widely explored; the phenomena in ice (or water), alcohols and acids have been studied in special detail. Nevertheless, data on hydrogen bonds in phenols are not so ample in literatures as those of alcohols and acids, at least so far as the crystalline state is concerned. In this connection the author has chosen, as the first of the series of investigation on the strength of hydrogen bond formed in crystals, a number of phenols of various kinds, and examined them following the procedure proposed in a previous paper[1]. The materials here examined include those the molecules of which have bulky substituents close to hydroxyl groups, preventing the formation of hydrogen bonds, such as *o*-hydroxydiphenyl or 2,4,6-tri-*tert*-butylphenol, and also 1- and 2-naphthols, which may be classified as phenols in a wider sense.

Experimental

The apparatus used for the measurement of sublimation pressures is the same as was used before[1].

Most of the materials dealt with in this paper are commercial products and purified by fractional sublimation before use. Four of them, i. e. 4-*tert*-butylphenol, 2-*tert*-butyl-4-methylphenol, 2-methyl-4-*tert*-butylphenol and 2,4,6-tri-*tert*-butylphenol were kindly sent by Professor M. Davies, Univ. Wales; these were purified in the same way as the others except 2-methyl-4-*tert*-butylphenol, which was fractionally distilled and measured in liquid state.

Results and Discussion

Sublimation Pressures. — Results of the measurements of sublimation pressures of thirteen phenols are shown in Tables I—XIII, respectively, together with vapor pressure equations obtained by the method of least squares.

TABLE I. SUBLIMATION PRESSURE OF *p*-HYDROXYDIPHENYL

T°K	P (mmHg) $\times 10^4$	T°K	P (mmHg) $\times 10^3$
327.6	3.88	337.7	1.10
329.1	4.54	339.4	1.33
329.8	4.94	342.6	1.84
331.2	5.67	345.6	2.46
335.1	8.48	347.6	3.02

$\log P(\text{mmHg}) = 12.056 - 5067.8/T$: m. p. 166°C

TABLE II. SUBLIMATION PRESSURE OF *o*-HYDROXYDIPHENYL

T°K	P (mmHg) $\times 10^3$	T°K	P (mmHg) $\times 10^3$
292.0	0.819	302.4	2.71
294.4	1.12	304.4	3.33
296.0	1.31	306.6	4.26
297.3	1.55	308.3	5.13
299.7	2.01	310.6	6.50
300.4	2.13	313.8	8.73

$\log P(\text{mmHg}) = 11.754 - 4331.0/T$: m. p. 59.0°C

1) A. Aihara, This Bulletin, **32**, 1242 (1959).

TABLE III. SUBLIMATION PRESSURE OF *p*-BENZYLPHENOL

T°K	P (mmHg) $\times 10^4$	T°K	P (mmHg) $\times 10^4$
313.8	2.75	323.8	8.48
315.4	3.29	326.1	10.9
317.1	4.07	328.3	14.2
318.5	4.71	330.7	18.1
320.0	5.65	332.1	21.1
321.8	6.76	335.0	29.8

$\log P\,(\text{mmHg}) = 12.600 - 5072.2/T$: m. p. 85.1°C

TABLE IV. SUBLIMATION PRESSURE OF *p*-*tert*-BUTYLPHENOL

T°K	P (mmHg) $\times 10^4$	T°K	P (mmHg) $\times 10^4$
281.0	4.57	289.7	13.6
281.5	5.04	293.5	21.3
282.3	5.38	295.5	27.5
283.8	6.72	299.0	40.5
285.1	7.78	301.2	52.4
287.8	10.8	303.6	67.9

$\log P(\text{mmHg}) = 12.332 - 4402.1/T$: m. p. 100.2°C

TABLE V. SUBLIMATION PRESSURE OF 2-*tert*-BUTYL-4-METHYLPHENOL

T°K	P (mmHg) $\times 10^3$	T°K	P (mmHg) $\times 10^3$
274.3	0.931	283.6	2.89
276.5	1.22	286.1	3.85
279.0	1.64	288.0	4.63
279.6	1.75	292.0	7.28
281.0	2.13	293.4	8.46

$\log P(\text{mmHg}) = 11.685 - 4035.9/T$: m. p. 53.4°C

TABLE VI. VAPOR PRESSURE OF 2-METHYL-4-*tert*-BUTYLPHENOL

T°K	P (mmHg) $\times 10^3$	T°K	P (mmHg) $\times 10^3$
275.3	0.692	286.9	2.59
277.4	0.895	288.9	3.33
279.5	1.15	292.6	4.78
282.9	1.69	294.5	5.74
285.6	2.32	297.2	8.33

$\log P(\text{mmHg}) = 11.199 - 3952.3/T$:
b. p. 125°C (15 mmHg)

TABLE VII. SUBLIMATION PRESSURE OF THYMOL

T°K	P (mmHg) $\times 10^3$	T°K	P (mmHg) $\times 10^3$
273.9	1.12	282.2	2.92
275.1	1.26	286.6	4.86
276.8	1.56	290.7	7.45
278.5	1.92	294.7	11.31

$\log P(\text{mmHg}) = 11.361 - 3921.0/T$: m. p. 49.5°C

TABLE VIII. SUBLIMATION PRESSURE OF 2,4,6-tri-*tert*-BUTYLPHENOL

T°K	P (mmHg) $\times 10^4$	T°K	P (mmHg) $\times 10^4$
291.7	3.07	301.6	9.55
293.4	3.63	304.5	12.9
295.2	4.52	306.2	15.6
297.4	5.83	309.7	22.9
299.7	7.63	312.9	30.9

$\log P(\text{mmHg}) = 11.507 - 4383.1/T$: m. p. 131.2°C

TABLE IX. SUBLIMATION PRESSURE OF *p*-FORMYLPHENOL

T°K	P (mmHg) $\times 10^4$	T°K	P (mmHg) $\times 10^3$
312.0	3.51	322.9	1.10
313.5	3.95	325.1	1.39
315.1	4.89	327.4	1.74
316.8	5.68	331.2	2.55
318.7	7.08	333.0	3.15
320.8	8.95	335.9	4.32

$\log P(\text{mmHg}) = 11.795 - 4762.3/T$: m. p. 118.5°C

TABLE X. SUBLIMATION PRESSURE OF *p*-ACETYLPHENOL

T°K	P (mmHg) $\times 10^4$	T°K	P (mmHg) $\times 10^4$
320.5	4.07	337.5	23.8
323.0	5.38	339.9	32.1
326.0	7.33	342.3	40.8
328.3	9.47	345.0	53.0
332.2	14.0	347.4	65.5
335.7	20.5	348.9	72.5

$\log P(\text{mmHg}) = 12.216 - 5003.5/T$: m. p. 109.8°C

TABLE XI. SUBLIMATION PRESSURE OF *p*-METHOXYPHENOL

T°K	P (mmHg) $\times 10^4$	T°K	P (mmHg) $\times 10^4$
278.8	3.55	288.7	12.8
279.6	3.95	292.1	19.8
282.1	5.33	293.9	25.4
283.4	6.48	295.7	30.9
285.4	8.38	297.9	40.4
286.9	10.2	300.1	52.9

$\log P(\text{mmHg}) = 13.132 - 4624.5/T$: m. p. 56.4°C

TABLE XII. SUBLIMATION PRERSURE OF 1-NAPHTHOL

T°K	P (mmHg) $\times 10^4$	T°K	P (mmHg) $\times 10^4$
298.2	5.37	309.3	21.0
299.6	6.49	311.3	26.6
300.2	7.00	312.0	28.3
301.3	8.05	314.3	36.1
302.4	9.25	315.1	38.9
303.3	10.3	317.6	51.5
304.8	12.4	319.6	62.7
305.3	13.1	321.8	76.7
306.9	15.9	323.4	89.0
307.9	18.1		

$\log P(\text{mmHg}) = 13.074 - 4873.0/T$,
(below 312.6°K):
$\log P(\text{mmHg}) = 11.526 - 4389.1/T$,
(above 312.6°K):
m. p. 97.0°C: t. p. 39.4°C

TABLE XIII. SUBLIMATION PRESSURE OF 2-NAPHTHOL

T°K	P(mmHg)$\times 10^4$	T°K	P(mmHg)$\times 10^4$
298.8	1.82	307.1	5.29
300.0	2.11	309.4	7.04
301.9	2.73	312.0	9.57
302.4	2.94	314.9	13.1
302.8	3.06	316.4	15.3
303.6	3.36	320.0	22.5
304.7	3.89	324.0	33.6
305.3	4.16	327.8	50.0
306.5	4.90	331.8	71.4

$\log P(\text{mmHg}) = 13.356 - 5108.6/T$, (below 312.3°K):
$\log P(\text{mmHg}) = 11.660 - 4578.9/T$, (above 312.3°K):
m. p. 123°C: t. p. 39.1°C

The linear relation between $\log P$ and $1/T$ has been found quite satisfactory for all the measurements except those of 1- and 2-naphthols, both of which have shown transitional changes of $\log P \sim 1/T$ curves at about 39°C. To confirm this change, careful measurements of sublimation pressures were made repeatedly, and from the intersections of two lines representing $\log P \sim 1/T$ relations for both phases, 39.4 and 39.1°C have been obtained as transition points of 1-naphthol and 2-naphthol, respectively (Fig. 1). As it is not proper to conclude the existence of a transition by the measurement of sublimation pressures alone, especially when the heat of transition is small, a thermal analysis of these substances is now in progress and the results will be published later.

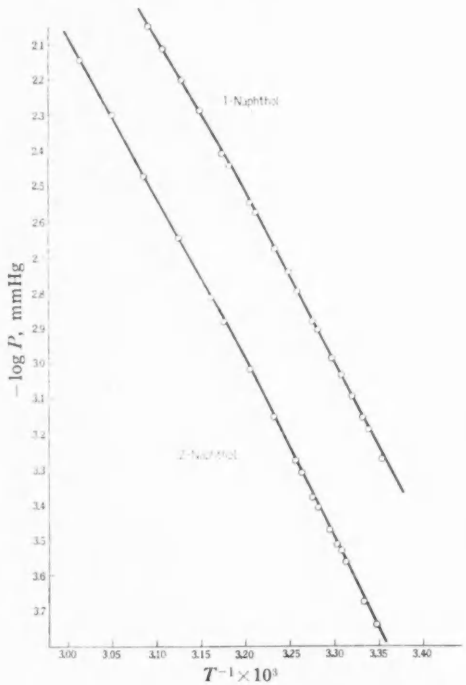


Fig. 1. Sublimation pressures of 1- and 2-naphthols.

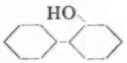
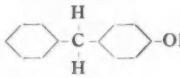
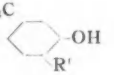
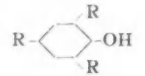
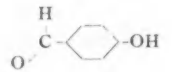
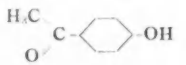
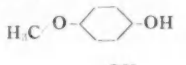
Balson[2] has also measured the sublimation pressure of thymol. However, his result, $\log P = 14.201 - 4766/T$, $\Delta H = 21.8$ kcal./mol., differs appreciably from the author's, the sublimation pressure being lower and the heat of sublimation being greater than the author's in the temperature range of the author's measurement. Considering the structure of this molecule Balson's value for the heat of sublimation of thymol seems to be too large.

Energy of Hydrogen Bond.—In Table XIV, the heats of sublimation of thirteen phenols, hypothetical lattice energies obtained assuming the additivity of lattice energies, and the energies of hydrogen bonds estimated by the procedure proposed before are shown by letters, ΔH, $\Delta H'$ and E, respectively. The changes of standard free energies at 298.2°K, $\Delta G^{298.2}$, and of entropies, ΔS, on sublimation are also shown in the table.

Let us first consider the case where the formation of OH···O bond seems rather difficult or almost impossible due to the presence of bulky substituted groups, such as phenyl and *tert*-butyl, in the vicinity of OH groups. Four compounds, i.e. *o*-hydroxydiphenyl, 2-*tert*-butyl-4-methylphenol, thymol and 2,4,6-tri-*tert*-butylphenol may fall in this category. As can be seen in Table XIV, the estimated values of hydrogen bonds for *o*-hydroxydiphenyl and 2-*tert*-butyl-4-methylphenol are negligibly small, being in fair agreement with the experimental results of infrared and ultraviolet absorption by Mecke[3], Coggeshall[4] and Josien[5]. According to Coggeshall[4], a phenol with one ortho position occupied by a *tert*-butyl and the other unoccupied, such as 2-*tert*-butyl-4-methylphenol, is partially hindered in forming a hydrogen bond. This means that one might expect, at least, a small

2) E. W. Balson, *Trans. Faraday Soc.*, **43**, 54 (1947).
3) R. Mecke and G. Rossmy, *Z. Elektrochem.*, **59**, 866 (1955).
4) N. D. Coggeshall and A. S. Glessner, Jr., *J. Am. Chem. Soc.*, **71**, 3150 (1949); N. D. Coggeshall and E. L. Saier, ibid., **73**, 5414 (1951).
5) M. L. Josien, N. L. Fuson and C. J. Lee, *Phys. Rev.*, **83**, 486 (1951).

TABLE XIV. VALUES OF THERMODYNAMIC FUNCTIONS AND ENERGIES OF HYDROGEN BOND

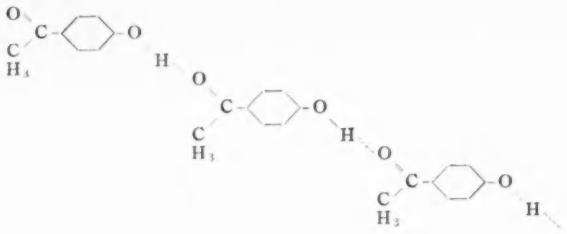
Compounds	ΔH kcal./mol.	$\Delta H'$ kcal./mol.	E kcal./mol.	$\Delta G^{298.2°}$ kcal./mol.	ΔS cal./deg. mol.
	23.19±0.12	20.0	3.2	10.67±0.23	42.0±0.4
	19.82±0.12	20.0	−0.2	7.70±0.24	40.6±0.4
	23.21±0.15	22.0	1.2	9.94±0.29	44.5±0.5
	20.14±0.08	16.5	3.6	7.24±0.16	43.3±0.3
	18.47±0.10	18.5	0.0	6.46±0.21	40.3±0.4
	18.09*±0.19	18.5	—	6.74*±0.38	38.1*±0.7
	17.94±0.09	16.5	1.4	6.37±0.18	38.8±0.3
	20.06±0.12	27.5	−7.4	8.29±0.24	39.5±0.4
	21.79±0.18	14.5	7.3	9.63±0.35	40.8±0.6
	22.90±0.16	16.5	6.4	10.16±0.31	42.7±0.5
	21.16±0.10	15.0	6.2	7.17±0.20	46.9±0.3
	22.30±0.17 (20.08±0.32)	17.5	4.8	8.39±0.33 (8.28±0.62)	46.6±0.6 (39.6±1.0)
	23.38±0.12 (20.95±0.18)	17.5	5.9	9.09±0.24 (8.97±0.35)	47.9±0.4 (40.2±0.6)

R = $C(CH_3)_3$, R' = $CH(CH_3)_2$

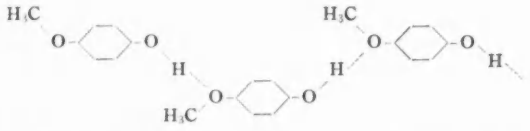
* For liquid state.

value of hydrogen bond energy for this compound instead of zero as shown in Table XIV. This discrepancy must be partly due to the difference in the states of the compound when it was examined, the one being solid and the other in solution, and partly due to the uncertainty of the method of estimation of hydrogen bond energy in this work. Thymol is a phenol with one ortho position occupied by an isopropyl group which is less powerful than *tert*-butyl in hindering the access of OH group of other molecules. Therefore, the energy of hydrogen bond in this compound, 1.4 kcal./mol., would be reasonable. A large negative value was obtained for 2,4,6-tri-*tert*-butylphenol. There will be no objection against believing that the OH group of this molecule is quite free from any intermolecular hydrogen bond, being protected by *tert*-butyl groups on both ortho positions, as was confirmed by Coggeshall[4] and Davies[6], by means of

6) M. Davies and R. J. Meakins, *J. Chem. Phys.*, **26**, 1584 (1957).



or



infrared technique and dielectric method in microwave region, respectively. Therefore, the large difference between ΔH and $\Delta H'$ for 2,4,6-tri-*tert*-butylphenol must be ascribed to the failure of the assumption, for this compound, of the additivity of lattice energy. This is understandable when the fact is taken into consideration that three *tert*-butyl groups of this molecule are bulky enough to screen a phenyl nucleus, to which they are attached, from the others, thereby causing the decrease of the effect of dispersive force due to the phenyl group to a greater extent. It is likely, therefore, that the *tert*-butyl groups are mainly responsible for dispersive attraction in this case, as was found with a system of SF_6 and CF_4, where the intermolecular attraction was discussed as due to halogen atoms of the molecules exclusively[7,8].

The heat of vaporization of 2-methyl-4-*tert*-butylphenol, 18.1 kcal./mol., is almost the same as the heat of sublimation of 2-*tert*-butyl-4-methylphenol, 18.5 kcal/mol.; this means that the OH···O bond in the crystal of the former should be stronger than that of the latter, as predicted from their molecular structures.

The hydrogen bond energies for *p*-hydroxydiphenyl and *p*-*tert*-butylphenol, 3.2 and 3.6 kcal./mol., respectively, are almost of the same order of magnitude, but somewhat smaller than the value obtained for phenol by Nitta and Seki, 4.5 kcal./mol.[9] This is probably due to a steric effect of large substituents in para positions rather than to any change of proton donating (or accepting) power of the OH groups. This effect is much more enhanced in the case of *p*-benzylphenol, obtained energy being 1.2 kcal./mol.

Comparatively large values of the energies of hydrogen bonds were obtained for *p*-formylphenol, *p*-acetylphenol and *p*-methoxyphenol, i.e. 7.3, 6.4 and 6.2 kcal./mol., respectively. It is interesting to note that these molecules have a possibility of making head-to-tail associations by hydrogen bonds.

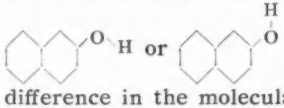
Then, the proton-donating power of OH and, at the same time, the proton-accepting power of O atoms of O=C and O-CH_3 groups must be increased appreciably, resulting in the increase of the strength of hydrogen bonds formed. As the crystal structures of these substances have not been analyzed as yet, a definite conclusion can not be drawn with regard to the mode of association of these molecules. Still, it will be quite safe to say that the OH···O bonds formed by these molecules are much stronger than those by other molecules mentioned above. The values for OH···O bonds obtained here can be compared with the energies of association of carboxylic acids in gaseous state, ~7 kcal./mol. (monomer), obtained by Taylor[10] and Nash[11]. Incidentally the pK_a values[12] of *p*-formylphenol, *p*-acetylphenol and *p*-methoxyphenol, which can be taken as the measure of proton-donating power of these molecules, 7.66, 7.95, 10.20, respectively, (in water at 25°C), support the correctness of the order of strength of

7) G. Thomaes, *J. chim. phys.*, **49**, 323 (1952).
8) J. S. Rowlinson, *J. Chem. Phys.*, **20**, 337 (1952).
9) I. Nitta and S. Seki, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **69**, 143 (1948); S. Seki, H. Chihara and K. Suzuki, "Hydrogen Bond", Iwanami-Shoten, Publishers, Tokyo (1956), p. 41.
10) M. D. Taylor, *J. Am. Chem. Soc.*, **73**, 315 (1951); M. D. Taylor and J. Bruton, ibid., **74**, 4151 (1952).
11) E. W. Johnson and L. K. Nash, ibid., **72**, 547 (1950); R. E. Lundin, F. E. Harris and L. K. Nash, ibid., **74**, 743, 4654 (1952).
12) E. A. Braud and F. C. Nachod, "Determination of Organic Structures by Physical Methods", Academic Press, Inc., New York (1955), p. 589, 598.

hydrogen bonds for these phenols as revealed here; the pK_a value of phenol is 9.95[12].

The hydrogen bond formed in the crystal of 2-naphthol is stronger than that in 1-naphthol, while the latter seems to be of the same order of strength as the bond in phenol[9]. A similar result was obtained by Nagakura[13] when he studied the proton-donating power of phenols and naphthols by the measurement of near ultraviolet absorption of these substances in appropriate solvents to which some proton-acceptors, such as methylacetate or dioxane were added; his values of the energies of OH···O bonds for phenol, 1-naphthol, and 2-naphthol are 5.3, 5.7 and 6.1 kcal./mol., respectively. These results are rather strange, as Nagakura pointed out, if the fact is considered that the extent of electron migration into the naphthyl ring from oxygen atom is almost of the same order as that into a benzene ring in the case of phenol, and therefore, that the pK_a values[12] and the dipole moments[14-16] of these three compounds are identical; pK_a=9.95, 9.85, 9.93 in water at 25°C, μ=1.5, 1.4, 1.5 D, respectively.

The author is inclined to presume that the main factor differentiating 1-naphthol from 2- with regard to the power of forming hydrogen bond is steric hindrance due to a hydrogen atom at 8-position in case of 1-naphthol. Thus, the OH group must be obliged to take only such a direction as to be opposite to the 8-position of the naphthyl nucleus. On the other hand, the OH group in 2-naphthol is quite free from such hindrance as mentioned above, and can take either of the directions,



, with a slight difference in the molecular structure.

In this connection a comment will be made of the transitions found with 1- and 2-naphthol. The fact of interest is that the transition points of these substances, 39.4 and 39.1°C, respectively, are very close to the melting point of phenol, 40.8°C, and that the heats of transition, 2.2 and 2.4 kcal./mol., respectively, are almost of the same order as the heat of fusion of phenol, 2.7 kcal./mol.[17] This would mean that the transitions and melting of the above substances might occur under the same mechanisms. It is most likely that intramolecular rotation about C–O bond[18] takes place at the melting point of phenol thereby leading to a less ordered state of liquid. As the O–H groups are bound to each other through chains of hydrogen bonds, a rotating part of the molecule will be mostly phenyl nucleus. That the change of entropy on melting at 40.8°C, 8.6 cal./deg. mol.[17], is almost the same as that of benzene at 5.5°C[17], and smaller than that of thiophenol, 10.5 cal./deg. mol. at −14.9 °C[17], may support the above argument. In the case of 1- and 2-naphthol, the onset of intramolecular rotations would lead to a transition in the crystalline states, but not to melting, because the effect of dispersive forces due to naphthyl rings is strong, as was found in the present experiment. Detaits will be published later.

Summary

The energies of hydrogen bonds formed in the crystalline state of twelve phenols have been estimated by a procedure proposed in a previous paper. The values of energy range from zero to 7 kcal./mol. depending upon the difference of molecular structures: the phenols with bulky substituents in the vicinity of OH groups are non- or weakly-hydrogen-bonded, while those with carbonyl or methoxy groups at para positions are strongly bonded presumably by head-to-tail association. The other phenols fall between the two extremes. Incidentally it is interesting that the highest values of OH···O bond are rather close to the energies of association of carboxylic acids in the gaseous state.

With 1- and 2-naphthols, a parallel relation between the transitions of the above substances and the melting of phenol has been pointed out.

The author is grateful to Professor M. Davies for sending some of the samples

13) S. Nagakura, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **74**, 153 (1953); ibid., **75**, 734 (1954); S. Nagakura and M. Gouterman, *J. Chem. Phys.*, **26**, 881 (1957).

14) R. Mecke and K. L. Schupp, *Z. Elektrochem.*, **52**, 54 (1948).

15) S. Nagakura and H. Baba, *J. Am. Chem. Soc.*, **74**, 5693 (1952).

16) R. J. W. Le Fèvre, "Dipole Moment", Methuen & Co., Ltd., London (1953), p. 133.

17) The Chemical Society of Japan, "A Handbook of Chemistry (Kagaku Binran)", Maruzen Co., Ltd., Tokyo (1958), p. 709, 710.

18) A potential barrier hindering the rotation of OH group in phenol is known to amount to 3.2 kcal./mol. [T. Nishikawa, *J. Jap. Chem.* (*Kagaku-no-Ryôiki*), **13**, 385 (1959)]; in 2,4,6-tri-*tert*-butylphenol it is 2.2 kcal./mol. [R. J. Meakins, *Trans. Faraday Soc.*, **52**, 320 (1956)].

dealt with in this work. The cost of the work was partly defrayed by the financial support of the Ministry of Education to which the author's thanks are due.

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Die absolute Konfiguration des Phyllodulcins

Von Hisao ARAKAWA

(Eingegangen am 30. April 1959)

Es sind verhältnismässig geringere Dihydroisocoumarinderivate in der Natur gefunden worden; als erstes hatten Asahina und Asano[1] 1931 die Struktur des Phyllodulcins (I), des Süßstoffs der Blätter von *Hydrangea macrophylla* Seringe var. *Thunbergii* MAKINO („Amacha"), festgestellt; seither sind Hydrangenol[1,2], Ochracin[3] (Mellein)[4,5], 3-Me-6-MeO-8-hydroxy-3,4-dihydroisocoumarin[6] und Bergenin[7] als Dihydroisocoumarinderivat charakterisiert und synthetisch sichergestellt worden.

Zur Aufklärung der Beziehung zwischen der optischen Aktivität und der absoluten Konfiguration der Verbindungen dieser Reihe, wählte der Verfasser als Repräsentanten das Phyllodulcin zuerst aus, und beabsichtigte die absolute Konfiguration ihres C-3-Atoms zu bestimmen.

Anderseits hatten vor einigen Jahren Hardegger et al.[8] durch erschöpfende Ozonisierung die absolute Konfiguration des (+)-Catechins, eines Naturstoffs von C_6-C_3-C_6-Gerüst, ähnlich wie I sichergestellt, also wünschte der Verfasser I dieser Methode zu unterwerfen.

Aber es ist schwer, optisch reinstes Präparat von I zu gewinnen. Das von Asahina et al.[1,9] als stärkst drehbares erhaltene Phyllodulcin zeigte den Schmerzp. 120° und $[\alpha]_D$ +67.7~69.70, aber da hatte man nur eine geringere Masse; und es ist dem Verfasser gelungen als stark drehbares Präparat Prismen von Schmerzp. 119~121°C und $[\alpha]_D$ +70.7~80.8°, ausserdem als schwach drehbare Kristalle von $[\alpha]_D$ +22.4° zu erhalten.

Deshalb wurde Phyllodulcin von $[\alpha]_D$ +70.7~80.8° in Essigsäure einer Ozonisierung unterworfen und Oxydation mit Peressigsäure, Entfernung der Oxalsäure und kontinuierliches Extrahieren mit Äther führten zu Äpfelsäure*. Die Veresterung der Säure mit Diazomethan lieferte Methylester von $[\alpha]_D$ +6.5°**, dessen IR-Spektrum mit solchem der authentischen DL-Äpfelsäure identisch ist. Schließlich führte Ammonolyse des Esters zu prismatischem Kristall von Schmerzp. 154~155°C, $[\alpha]_D$ +56.7°. Durch Mischprobe, Vergleichen des IR-Spektrums mit solchem des authentischen Präparates von *R*-Äpfelsäure und spezifische Drehung, ist es sichergestellt, daß das *R*-Äpfelsäure diamid gewonnen worden ist.

Mit der Isolierung der *R*-Äpfelsäure (II) ist es nun bestimmt, daß die absolute Konfiguration des C 3 in Phyllodulcin *R*-Konfiguration ist.

1) Y. Asahina und J. Asano, *Ber.*, **62**, 171 (1929); **63**, 429, 2059 (1930); **64**, 1252 (1931).

2) Hydrangenol: Inhaltstoff von *Hydrangea Hortensia* DC. var. *Otakusa* MAXIM.

3) Stoffwechselprodukt von *Aspergillus ochraceus*: E. Nishikawa, *J. Agric. Soc. Japan* (*Nippon Nôgei-kagaku Kaishi*), **9**, 772, 1059 (1933).

4) Stoffwechselprodukt von *Aspergillus melleus* YUKAWA: T. Yabuta und Y. Sumiki, ebenda, **9**, 1264 (1933); **10**, 703 (1934).

5) J. Blair and G. T. Newbold, *J. Chem. Soc.*, **1955**, 2871.

6) Inhaltstoff der in der Kühle bewahrten Mohren; E. Sondheimer, *J. Am. Chem. Soc.*, **79**, 5036 (1957).

7) J. E. Hay und L. J. Haynes, *J. Chem. Soc.*, **1958**, 2231.

8) E. Hardegger, H. Gempeler und A. Zürst, *Helv. Chim. Acta*, **40**, 1819 (1957).

9) Y. Asahina und S. Ueno, *J. Pharm. Soc. Japan* (*Yakugaku Zasshi*), Nr. **408**, 146 (1916); *Chem. Abstr.*, **10**, 1524 (1916).

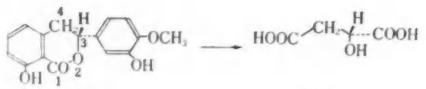
* Papierchromatographisch charakterisierte man als Äpfelsäure. Noch dazu wurde aus dem Kristall von $[\alpha]_D$+22.4° Äpfelsäure als Kristalle erhalten und ihre IR-Spektren stimmten mit solchen der authentischen DL-Äpfelsäure überein und ihre Drehungen in 10-proz. Ammoniummolybdat zeigten links drehend bis $[\alpha]_D$ −46.3°. Darum ist die erhaltene Säure ein Gemisch von DL-Körper mit wenigem D-Körper, denn es ist bekannt[10], daß der Drehungssinn einer optisch aktiven Äpfelsäure sich in der Lösung von Ammoniummolybdat umkehrt und ihr Drehungsvermögen mehr als 10-mals vergrößert worden ist.

10) H. D. Dakin, *J. Biol. Chem.*, **59**, 9 (1924).

** Aus dem Phyllodulcin von $[\alpha]_D$+22.4° wurde Methylester von $[\alpha]_D$+2.3° erhalten. (s. Versuche).

TABELLE I

Fraktion (Ausbeute)	Schmerzp. °C	Optische Aktivität (in Aceton)	Analysenwert	Ber. für $C_{16}H_{14}O_5$
A (11.7 g)	129～130	$[\alpha]_D^{16}$ +22.4° (c=1.16)	C 67.27 H 5.10	
B (1.0 g)	118～119	$[\alpha]_D^{19}$ +71.7° (c=1.14)	C 67.06 H 5.10	C 67.12 H 4.93
C (2.8 g)	119～121	$[\alpha]_D^{13}$ +70.7° (c=1.02)	C 67.16 H 5.08	
D (1.7 g)	120～121	$[\alpha]_D^{17}$ +80.8° (c=1.14)	C 66.97 H 5.13	



(I) (II)

Beschreibung der Versuche

Extrahieren des Phyllodulcins.—Der zu 5.5 kg käufliche „Amacha" wurde mit essigsäurehaltigem wässer. Methanol extrahiert (einmal, einige Tage lang). Nach im Vakuum Abdampfen des Methanols ausgeschiedene grüne rohe Kristalle wurden mit Äther, Chloroform, Äthanol und Methanol gereinigt. Die Kristalle jeder Fraktion wurden mehrmals fraktioniert aus Äthanol umkristallisiert. Es wurden die Prismen erhalten, die rein süß schmecken (Tabelle I).

Die IR-Spektren von B, C, D in Nujol stimmen überein. Die IR-Spektren von A und B in Chloroform sind identisch.

Ozonspaltung von Fraktion A $[\alpha]_D$ +22.4°.—Durch eine Lösung von Fraktion A (10 g) in 100 ccm 90-proz. Essigsäure wurde bei 5°C Ozon geleitet. Die Lösung färbte sich bald dunkelbraun und hellte dann auf, schließlich wurde sie nach 67 Stdn. ganz farblos und teils kristallisierte Oxalsäure, die bei 98～100°C schmolz und durch Mischprobe mit authentischem Präparat identifiziert wurde. Nach Zugabe von 15 ccm Perhydrol wurde die Lösung 24 Stdn. lang stehen gelassen und mit 50 ccm Wasser versetzt, dann wurde die Lösung nach Hardegger et al.[8] behandelt und von Oxalsäure befreit und dann im Vakuum eingedampft. Der erhaltene Rückstand wurde nach Zugabe von Wasser wiederholt im Vakuum eingedampft, und der getrocknete Rückstand (6 g) in warmem Wasser gelöst, und dann mit Äther kontinuierlich extrahiert.

Nach Abdampfen von Äther und nack Trocknen dann abfiltriert. Der erhaltene gelbe Rückstand betrug 470 mg. Dreimaliges Umkristallisieren aus Methanol gab 60 mg fast farblose Prismen von Schmerzp. 154～155°C, $[\alpha]_D^{13}$ +56.7° (c=1.18 in Methanol).

war der Extrakt größtenteils kristallisiert. Fraktioniertes Umkristallisieren aus Essigester gab farblose Kristalle (Tabelle II).

Nach Trocknen des Kristalls von Schmerzp. 113～116°C bei 80°C im Vakuum.

$C_4H_6O_5$

Ber. C 35.83 H 4.51
Gef. C 35.85 H 4.63

Die Mutterlauge wurde in Vakuum-Exsiccator abgedampft, wonach der Rückstand in Methanol gelöst, mit Diazomethan verestert und mit Natriumsulfat getrocknet. Nach Vorlauf von Kochp. 62°C/2 mmHg wurde 490 mg Hauptfraktion von Kochp. 110～111°C/10 mmHg, $[\alpha]_D^{13}$ +2.7° (c=16.3 in Methanol) erhalten.

$C_6H_{10}O_5$

Ber. C 44.44 H 6.22
Gef. C 44.19 H 6.42

Das IR-Spektrum stimmte mit solchem des authentischen DL-Äpfelsäuredimethylesters von Kochp. 115～117°C/14 mmHg (in CS_2, CCl_4) überein.

Abbau der Fraktionen B, C und D von $[\alpha]_D$ +70.7～80.8° mit Ozon und Isolierung von *R*-Äpfelsäure als Diamid aus dem Ätherextrakt.—Durch eine Lösung von 5.2 g Kristalle (0.9 g B+2.7 g C+1.6 g D) in 50 ccm 95-proz. Essigsäure wurde 3-proz. Ozon 31 Stdn. lang eingeleitet, wonach sie mit 7.5 ccm Perhydrol versetzt, 18 Stdn. lang stehen gelassen und dann wie oben behandelt, mit Äther 20 Stdn. extrahiert. Der erhaltene Rückstand wog 3.3 g und sein Papierchromatogramm (Xylol, Phenol, 85-proz. Ameisensäure, 5:5:2)[11] lieferte die Flecke der Äpfelsäure. Seine Methanollösung wurde dann verestert. Die Destillation des getrockneten Methylesters ergab bei 111～112°C/10 mmHg 700 mg von $[\alpha]_D^{\infty}$ +6.5° (c=12.89). Das IR-Spektrum stimmt mit solchem von DL-Äpfelsäuredimethylester überein.

666 mg Methylester wurde in verzweigtem Reagenzrohr (unter Abkühlung durch eine Mischung von fester Kohlensäure mit Äthanol) mit 12 ccm von verflüssigtem Ammoniak aus der Bombe versetzt und dann das Reagenzrohr in einem Autoklav geschlossen. Nach Stehenlassen bei Zimmertemperatur 24 Stdn. lang, dampfte man Ammoniak ab und mischte mit Äther und

TABELLE II

Schmerzp. °C	Ausbeute g	Spezifisches Drehungsvermögen in 10-proz. Ammoniummolybdat
131～132	0.3	—***
125～127	0.2	$[\alpha]_D^{13}$ −4.9° (c=3.05)
119～121	0.4	$[\alpha]_D^{25}$ −11.7° (c=5.03)
113～116	0.1	$[\alpha]_D^{12}$ −46.3° (c=1.12)

*** Misch-Schmerzp. mit authentischer DL-Äpfelsäure: 131～132°C.

11) Vgl. H. Kalbe, *Z. physiol. Chem.*, **297**, 19 (1954).

$C_4H_5O_3N_2$

Ber.	C 36.36	H 6.10	N 21.20
Gef.	C 36.59	H 6.34	N 21.07

Misch-Schmerzp. mit authentischem Präparat[12] von Schmerzp. 156°C, $[\alpha]_D$ +60.3° zeigte 154~156°C. Beide IR-Spektren sind praktisch ganz identisch.

12) Herrn Ryonosuke Yoshida, Naturwissenschaftliche Fakultät, Universität Osaka, sei für die freigebige Überlassung des Präparates von *R*-Apfelsäurediamid gedankt.

Herrn Prof. Dr. Masao Nakazaki danke ich bestens für sein reges Interesse an der vorliegenden Arbeit und seine Unterstützung durch wertvolle Hinweise.

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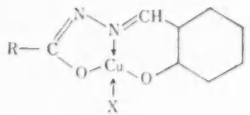
*Über die Kupferkomplexsalze der Salicylaldehyd-acylhydrazone**

Von Hiroshi OHTA

(Eingegangen am 30. Mai 1959)

In der vorangehenden Mitteilung[1] wurde gezeigt, daß die Salicylaldehyd-aroylhydrazone, welche tuberkulostatische Wirkung besitzen[2], mit 2-wertigem Kupferion im ammoniak-alkalischen Medium die Kupferkomplexsalze der Formel I liefern (I[A]).



I

[A] R=Arylreste, X=NH_3 od. C_5H_5N.
[B] R= X=NH_3 od. 0.

(1)	—H	(7)	$-(CH_2)_4\cdot CH_3$
(2)	$-CH_3$	(8)	$-(CH_2)_6\cdot CH_3$
(3)	$-CH_2\cdot CH_3$	(9)	$-(CH_2)_8\cdot CH_3$
(4)	$-(CH_2)_2\cdot CH_3$	(10)	$-(CH_2)_{14}\cdot CH_3$
(5)	$-(CH_2)_3\cdot CH_3$	(11)	$-CH_2\cdot C_6H_5$
(6)	$-CH_2\cdot CH\cdot (CH_3)_2$	(12)	$-CH_2\cdot O\cdot C_6H_5$

Werden die Aroylreste mit den Acylresten ersetzt, so lassen sich die Salicylaldehyd-acylhydrazone erhalten, die auch, als Chemotherapeutica, in Frage kommen. Durch Anfügen der Acylreste mit längeren Ketten sollen Salicylaldehyd-acylhydrazone lipophile Eigenschaft gewinnen, die den Angriff der Substanzen auf wachsgepanzerte Bakterien erleichtern könnte.

In der vorliegenden Mitteilung sollen die Salicylaldehyd-acylhydrazone, worunter einige noch nicht berichtet worden sind, und deren Kupferkomplexsalze beschrieben werden.

Neue Acylhydrazine und Salicylaldehyd-acylhydrazone wurden in üblicher Weise dargestellt; Acylhydrazine durch Erhitzen der Fettsäureester mit Hydrazinhydrat, Salicylaldehyd-acylhydrazone durch Gemisch des Salicylaldehydes und der Acylhydrazine. Als Ausgangsstoffe für die Komplexsalzdarstellung wurden Salicylaldehyd-formylhydrazon, -acetylhydrazon, -propionylhydrazon, -*n*-butyrylhydrazon, -*n*-valerylhydrazon, -*i*-valerylhydrazon, -*n*-capronylhydrazon, -*n*-caprylylhydrazon, -*n*-caprinylhydrazon, -*n*-palmitylhydrazon, -phenylacetylhydrazon und -phenoxyacetylhydrazon herangezogen. Alle diese Hydrazone sind schneeweiß, und in Äthanol und anderen organischen Lösungsmitteln sehr leicht löslich; sie lassen sich aus Äthanol leicht umkristallisieren.

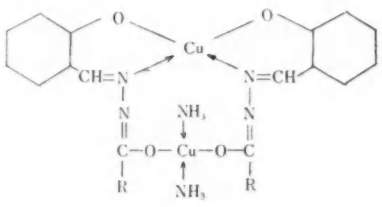
Die Komplexsalze wurden, wie im Versuchsteile näher beschrieben, durch Gemisch der Hydrazone in Äthanol und des Kupferacetats in wässrigem Ammoniak dargestellt. Sie bilden hell- bzw. dunkelgrüne Kristalle, und nach den analytischen Daten kommt ihnen eine allgemeine empirische Formel $[C_9H_5O_2N_2RCu\cdot(NH_3)_{0\text{ oder }1}]$ zu. Die Komplexsalze des Salicylaldehyd-*n*-palmitylhydrazons, -phenylacetylhydrazons und -phenoxyacetylhydrazons enthalten je 1 Mol. Ammoniak und geben es (mit Ausnahme vom Komplexsalze des Salicylaldehyd-phenoxyacetylhydrazons) beim Erhitzen im Vakuum leicht ab; deren

* Organische Metallkomplexsalze III. Vorgetragen in Kyoto auf der XII. Jahresversammlung der Japanischen Chemischen Gesellschaft, am 3. April 1959.

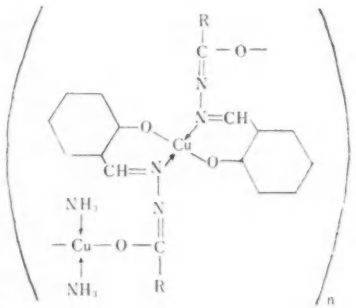
1) II. Mitteilung: H. Ohta, Dieses Bulletin, **31**, 1056 (1958).

2) Ng. Ph. Buu-Hoï und Mitarbb., *J. Chem. Soc.*, **1953**, 1358.

Farbe schlägt vom Hellgrün nach Olivgrün um. Das Ammoniak muß daher koordinativ mit dem Kupferatom gebunden sein. Aus Rücksicht auf die Koordinationszahl des Kupfers und die Struktur des Liganden können diese Komplex salze mit der Formel I formuliert werden. Die Formeln II und III werden als unwahrscheinlich ausgeschlossen, weil 1) die Ausbildung der



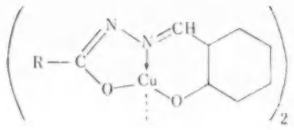
II



III

Salze von der Formel II bzw. III sterisch nicht oder sehr schwer möglich ist, und 2) die Salze der Formel III nur als amorphes Pulver erhalten würden.

Die anderen übrigen Komplexsalze enthalten kein Ammoniak und sind dunkelgrün gefärbt. Diese und diejenigen, die durch Erhitzen im Vakuum das Ammoniak verloren haben, gehören zu den „Kupferkomplexsalzen der Koordinationszahl 3". Von ihnen sind die des Salicylaldehyd-*n*-caprinylhydrazons und -*n*-palmitylhydrazons in Campher löslich. Die Molekulargewichte beider Salze wurden nach Rast durch die kryoskopische Methode bestimmt. Die Resultate zeigten, daß sie dimer sind. Da die Formel II undenkbar ist, könnten diese Komplexsalze mit der Formel IV zum Ausdruck gebracht werden. Wahrscheinlich zwischen den beiden Kupferatomen wäre irgendeine Art Wechselwirkung vorhanden. Auch die magnetischen Messungen



IV

wurden mit diesen zwei Verbindungen in festem Zustand ausgeführt. Wegen der technischen Schwierigkeiten — *N*-Salicyliden-*N'*-*n*-palmityl-hydrazino-kupfer (II) konnte nicht, *N*-Salicyliden-*N'*-*n*-caprinil-hydrazino-kupfer(II) konnte nur äußerst schwer, pulverisiert werden — wurden jedoch keine befriedigenden Ergebnisse erhalten.

Beschreibung der Versuche

Acylhydrazine und Salicylaldehyd-acylhydrazone. —Acylhydrazine können in üblicher Weise durch Kochen von Fettsäureestern mit etwas überschüssigem Hydrazinhydrat leicht synthetisiert werden. Die neuen Acylhydrazine wurden als Salicylidenderivate (Salicylaldehydacylhydrazone) charakterisiert.

Salicylaldehyd-acylhydrazone werden durch Gemische berechneter Mengen Salicylaldehyd und Acylhydrazine in Äthanol dargestellt und daraus umkristallisiert.

Salicylaldehyd-acetylhydrazon. — Weiße Nadeln. Schmp. 201~202°C (unkorr.).

$C_9H_{10}O_2N_2$

Ber. C 60.66 H 5.66 N 15.72
Gef. C 60.84 H 5.81 N 15.71

Salicylaldehyd-n-butyrylhydrazon.—Weiße, feine Nadeln. Schmp. 138~139°C (unkorr.).

$C_{11}H_{14}O_2N_2$

Ber. C 64.06 H 6.84 N 13.58
Gef. C 64.21 H 7.01 N 13.64

Salicylaldehyd-n-valerylhydrazon.—Weiße, feine Nadeln. Schmp. 140~141°C (unkorr.).

$C_{12}H_{16}O_2N_2$

Ber. C 65.43 H 7.32 N 12.72
Gef. C 65.68 H 7.18 N 12.79

Salicylaldehyd - n - capronylhydrazon. — Weiße Nadeln. Schmp. 123~124°C (unkorr.).

$C_{13}H_{18}O_2N_2$

Ber. C 66.64 H 7.74 N 11.96
Gef. C 66.86 H 7.71 N 12.09

Salicylaldehyd-n-caprylhydrazon.—Weiße, zarte Nadeln. Schmp. 104~105°C (unkorr.).

$C_{15}H_{22}O_2N_2$

Ber. C 68.67 H 8.45 N 10.68
Gef. C 68.94 H 8.22 N 10.67

Salicylaldehyd - n - caprinylhydrazon. — Weiße Nadeln. Schmp. 101~102°C (unkorr.).

$C_{17}H_{26}O_2N_2$

Ber. C 70.31 H 9.02 N 9.65
Gef. C 70.10 H 8.92 N 9.64

Salicylaldehyd - phenoxyacetylhydrazon. — Weiße, feine Nadeln. Schmp. 171~172°C (unkorr.).

$C_{15}H_{14}O_3N_2$

Ber. C 66.66 H 5.22 N 10.36
Gef. C 66.53 H 5.09 N 10.25

Kupferkomplexsalze.—*N-Salicyliden-N'-formyl-hydrazino-kupfer (II)*.—Man gibt 4 ccm Ammoniakwasser (28%) zur Lösung von 164 mg Salicylaldehyd-formylhydrazon in 6 ccm Äthanol. Die Farbe der Lösung wird gelb. Zu dieser gelben Lösung setzt man eine Lösung von 200 mg Kupferacetat (Monohydrat) in 5 ccm Äthanol-Ammoniakwasser-Gemische (Volumverhältnis: 2 : 1) hinzu. Die so entstandene, grünschwarze Lösung engt man auf dem Wasserbade allmählich ein. Dunkelgrüne Nädelchen. Man kann sie durch Lösen in Alkohol-Ammoniakwasser-Gemisch und Eindunsten der Lösung auf dem Wasserbade reinigen.

$C_9H_6O_2N_2$

Ber. C 42.57 H 2.68 N 12.41 Cu 28.15
Gef. C 42.69 H 3.14 N 12.27 Cu 28.00

N-Salicyliden-N'-acetyl-hydrazino-kupfer(II).—Man fügt zur Lösung von 178 mg Salicylaldehyd-acetylhydrazon in 10 ccm Äthanol eine Lösung von 200 mg Kupferacetat in 5 ccm Ammoniakwasser zu. Es entsteht sofort eine grünschwarze, klare Lösung, die man auf dem Wasserbade einengt. Dunkelgrüne, glänzende Nädelchen.

$C_9H_8O_2N_2Cu$

Ber. C 45.09 H 3.36 N 11.69 Cu 26.51
Gef. C 44.87 H 3.41 N 11.78 Cu 26.37

N-Salicyliden-N'-propionyl-hydrazino-kupfer(II).—Zu einer Lösung von 192 mg Salicylaldehyd-propionyl-hydrazon in 10 ccm Äthanol fügt man eine Lösung von 200 mg Kupferacetat in 5 ccm Ammoniakwasser zu und engt die so erhaltene, grünschwarze, klare Lösung auf dem Wasserbade allmählich ein. Dunkelgrüne Nädelchen.

$C_{10}H_{10}O_2N_2Cu$

Ber. C 47.33 H 3.97 N 11.04 Cu 25.04
Gef. C 47.23 H 4.29 N 11.26 Cu 24.98

N-Salicyliden-N'-n-butyryl-hydrazino-kupfer(II).—Man fügt zur Lösung von 206 mg Salicylaldehyd-*n*-butyryl-hydrazon in 10 ccm Äthanol, 200 mg Kupferacetat gelöst in 5 ccm Ammoniakwasser zu. Eine schwarzgrüne Lösung entsteht, die man auf dem Wasserbade einengt. Grünschwarze Kristallle.

$C_{11}H_{12}O_2N_2Cu \cdot 1/2\,H_2O$

Ber. C 47.73 H 4.73 N 10.12 Cu 22.96
H_2O 3.25
Gef. C 47.57 H 4.68 N 9.97 Cu 23.24
H_2O 3.28

N-Salicyliden-N'-n-valeryl-hydrazino-kupfer(II).—Man gibt zur Lösung von 220 mg Salcylaldehyd-*n*-valeryl-hydrazon in 10 ccm Äthanol eine Lösung von 200 mg Kupferacetat in 5 ccm Ammoniakwasser. Es entsteht eine schwarzgrüne, klare Lösung die man auf dem Wasserbade allmählich einengt. Dunkelgrüne, fast schwarz erscheinende Plättchen.

$C_{12}H_{14}O_2N_2Cu$

Ber. C 51.15 H 5.01 N 9.94 Cu 22.55
Gef. C 51.02 H 5.09 N 9.73 Cu 22.71

N-Salicyliden-N'-i-valerly-hydrazino-kupfer(II).—Dies wird gleicherweise wie beim *N*-Salicyliden-*N'-n*-valeryl-hydrazino-kupfer(II) dargestellt. Dunkelgrüne, fast schwarze, glänzende Plättchen.

$C_{12}H_{14}O_2N_2Cu \cdot H_2O$

Ber. C 48.07 H 5.38 N 9.34 Cu 21.19
H_2O 6.01
Gef. C 48.86 H 5.54 N 9.48 Cu 21.25
H_2O 5.98

N-Salicyliden-N'-n-capronyl-hydrazino-kupfer(II).—Dies wird ähnlich wie bei den obenerwähnten Komplexsalzen, aus 234 mg Salicylaldehyde-*n*-capronylhydrazon in 10 ccm Äthanol und 200 mg Kupferacetat in 5 ccm Ammoniakwasser dargestellt. Schwärzlich-dunkelgrüne Kristalle.

$C_{13}H_{16}O_2N_2Cu \cdot 1/2\,H_2O$

Ber. C 51.22 H 5.62 N 9.19 Cu 20.84
H_2O 2.96
Gef. C 51.31 H 5.86 N 9.00 Cu 20.63
H_2O 3.00

N-Salicyliden-N'-n-caprylyl-hydrazino-kupfer(II).—Man trägt in eine Lösung von 262 mg Salicylaldehyd-*n*-caprylylhydrazon in 10 ccm Äthanol, 200 mg Kupferacetat gelöst in 5 ccm Ammoniakwasser ein und fügt zur so erhaltenen, grünschwarzen Lösung 15 ccm Ammoniakwasser allmählich zu. Grüne, zarte Nadeln, die aber keine stöchiometrische Menge Ammoniak enthalten. Analysiert wurde eine Substanzprobe, die durch 1-stündiges Erhitzen auf 110～120°C/25 mmHg als braunischgrünes Pulver erhalten worden war.

$C_{15}H_{20}O_2N_2Cu$

Ber. C 55.63 H 6.22 N 8.65 Cu 19.62
Gef. C 55.51 H 6.48 N 8.66 Cu 19.52

N-Salicyliden-N'-n-caprinyl-hydrazino-kupfer(II).—Man fügt zur Lösung von 290 mg Salicylaldehyd-*n*-caprinyl-hydrazon in 5 ccm Äthanol eine Lösung von 200 mg Kupferacetat in 5 ccm ammoniakwasser zu. Dunkelgrüne, zarte Nädelchen.

$C_{17}H_{24}O_2N_2Cu$

Ber. C 58.02 H 6.87 N 7.96 Cu 18.05
Gef. C 57.78 H 7.02 N 7.84 Cu 17.94

N-Salicyliden-N'-n-palmityl-hydrazino-monoammin-kupfer(II)-monohydrat.—Fügt man zur Lösung von 375 mg Salicylaldehyd-*n*-palmitylhydrazon in 10 ccm Äthanol eine Lösung von 200 mg Kupferacetat in 5 ccm Ammoniakwasser zu, so scheiden sich sogleich graugrüne Kristalle aus, die man aus Äthanol-Ammoniakwasser-Gemische (Volumverhältnis: 2 : 1) umkristallisiert. Hellgraugrüne, zarte Nadeln.

$C_{23}H_{36}O_2N_2 \cdot NH_3 \cdot Cu \cdot H_2O$

Ber. C 58.63 H 8.77 N 8.92 Cu 13.49
NH_3+H_2O 7.44
Gef. C 58.93 H 8.87 N 8.80 Cu 13.15
NH_2+H_2O (1 Stunde auf 110°C/25 mmHg) 7.54

N-Salicyliden-N'-n-palmityl-hydrazino-kupfer(II).—Man erhitzt *N*-Salicyliden-*N'*-*n*-palmityl-hydrazino-monoammin-kupfer(II)-monohydrat eine Stunde auf 110°C/25 mmHg. Dunkelgrüne Nadeln.

$C_{23}H_{36}O_2N_2Cu$

Ber. C 63.35 H 8.32 N 6.42 Cu 14.57
Gef. C 63.31 H 8.56 N 6.42 Cu 14.23

N-Salicyliden-N'-phenylacetyl-hydrazino-monoammin-kupfer(II)-monohydrat.—Man fügt zur Lösung von 255 mg Salicylaldehyd-phenylacetylhydrazon in 10 ccm warmem Äthanol, eine Lösung von 200 mg Kupferacetat in 5 ccm Ammoniakwasser zu.

Tabelle

Verbindung und Molekulargewicht ber.	Einwaage Komplex mg	Einwaage Campher mg	ΔT °C	Molekulargewicht gef.
N-Salicyliden-*N'*-*n*-caprinyl-hydrazino-kupfer(II) 351.9×2=703.8	3.6	40.4	5	713
	3.3	55.6	3.5	678
N-Salicyliden-*N'*-*n*-palmityl-hydrazino-kupfer(II) 436.1×2=872.2	4.5	41.8	5	861
	4.1	43.1	4	951
	2.7	20.9	6	864

Man engt die so erhaltene, grünschwarze, klare Lösung auf dem Wasserbade ziemlich stark ein und läßt erkalten. Graulich braungrüne Nädelchen.

$C_{15}H_{12}O_2N_2 \cdot NH_3 \cdot Cu \cdot H_2O$

Ber. C 51.35 H 4.88 N 11.98 Cu 18.11 NH_3+H_2O 9.99

Gef. C 51.78 H 5.00 N 11.90 Cu 18.00 NH_3+H_2O (1 Stunde auf 110°C/25 mmHg) 9.90

Das wasser- und ammoniakfreie Salz ist bräunlich grün.

N-Salicyliden-N'-phenoxyacetyl-hydrazino-monoammin-kupfer(II).—Man fügt zur Lösung von 270 mg Salicylaldehyd-phenoxyacetylhydrazon in 15 ccm warmem Äthanol, 200 mg Kupferacetat gelöst in 5 ccm Ammoniakwasser zu und läßt erkalten. Aus der anfangs entstandenen, grüschwarzen, klaren Lösung scheiden sich feine, hellbraune Nadeln aus, die auch beim Erhitzen unter vermindertem Drucke (2 Stunden auf 130~140°C/25 mmHg) keinen Gewichtsverlust erleiden.

$C_{15}H_{12}O_3N_2 \cdot NH_3 \cdot Cu$

Ber. C 51.64 H 4.33 N 12.05 Cu 18.21

Gef. C 51.46 H 4.47 N 11.87 Cu 18.30

Molekulargewichtsbestimmungen an den Komplexsalzen.—Die Molekulargewichtsbestimmungen wurden nach der Rastschen Methode ausgeführt, wobei die Gefrierpunkte gemessen wurden. Brauchbare Ergebnisse konnten aus Löslichkeitsgründen nur mit dem *N*-Salicyliden-*N'*-*n*-caprinyl-hydrazino-kupfer(II) und dem *N*-Salicyliden-*N'*-*n*-palmityl-hydrazino-kupfer(II) erzielt werden; bei ersterem machte sich Anwendung eines 20-fachen Campherüberschusses nötig.

Die Tabelle zeigt die erhaltenen Werte:

Meinem Lehrer, Herrn Professor Dr. Tokuichi Tsumaki danke ich herzlich für die Unterstützung und Förderung dieser Arbeit. Herrn Dr. Yasushi Koga (Laboratorium für Physikalische Chemie, Chemisches Institut, Naturwissenschaftliche Fakultät, Kyushu Universität) bin ich für die magnetischen Messungen zu großem Dank verpflichtet. Herrn Michio Shido und Frl. Sachiko Indo (Laboratorium der Elementaranalyse, Kyushu Universität) verdanke ich die Durchführung der C-, H- und N-Bestimmungen.

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Darstellung von o-Diacetylbenzol durch Diels-Alder-Reaktion

By Eturô MAEKAWA

(Eingegangen am 1. August, 1959)

o-Diacylbenzole sind nicht nur als Ausgangsprodukte der Naphthochinonsynthese[1] von präparativer Bedeutung, sondern bilden auch wegen ihrer intensiven Farbreaktion mit Aminosäuren[2,3] und auch mit primären Aminen[4,5] sehr interessante Verbindungen. Die Farbreaktion von *o*-Diacylbenzolen ist so stark, daß man mit ihnen z. B. 20~50 γ Aminosäuren[2] oder 1 γ aromatische primäre Amine[4] auf Papierchromatogrammen einwandfrei nachweisen kann. Sie lassen sich darstellen aus *o*-*n*-Alkylacylbenzolen durch Oxydation mit Permanganat[1,2] oder aus 3-Alkylphthaliden durch Umsetzung mit Alkylmagnesiumhalogeniden und durch direkte Oxydation

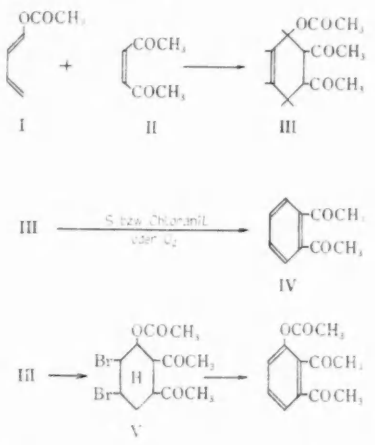
1) F. Weygand, H. Weber und E. Maekawa, *Chem. Ber.*, **90**, 1879 (1957).
2) R. Riemenschneider und C. Weygand, *Monatsh. Chem.*, **86**, 201 (1955).
3) W. Winkler, *Chem. Ber.*, **81**, 256 (1948).
4) F. Weygand, H. Weber und G. Eberhard, *Angew. Chem.*, **66**, 680 (1954).
5) F. Weygand, H. Weber, E. Maekawa und G. Eberhard, *Chem. Ber.*, **89**, 1994 (1956).

des gebildeten Magnesiumsalzes der 1-Oxy-1.3-dialkylphthalane mit Permanganat[1]. Obgleich die Darstellung von *o*-Diacylbenzolen stark verbessert wurde[4,5], geht sie noch immer in ziemlich schlechter Ausbeute vor sich. Außerdem sind die Oxydationsbedingungen bei der ersten Methode so stark, daß diese auf die Ausgangsprodukte mit leicht oxydierbaren Substituenten schwer anwendbar ist. Das zweite Verfahren wird unter milderen Bedingungen durchgeführt, liefert aber nur unreine Produkte.

Wie von F. Weygand u. a. berichtet wurde[1], aromatisiert das Addukt aus 1-Acetoxybutadien-(1.3)[6] und 2.3-Dimethoxy-*p*-benzochinon in siedendem Alkohol automatisch unter Abspaltung von Essigsäure und Wasserstoff zu 2.3-Dimethoxynaphthochinon-(1.4). Diese Tatsache erweckte die Hoffnung, *o*-Diacetylbenzol aus 1-Acetoxybutadien-(1.3) und $\alpha.\beta$-Diacetyläthylen[7,8] durch Diensynthese herstellen zu können. 1-Acetoxybutadien-(1.3) und $\alpha.\beta$-Diacetyläthylen geben beim Kochen der alkoholischen Lösung in guter Ausbeute des Addukt, 3-Acetoxy-1.2.3.6-tetrahydro-1.2-diacetylbenzol, das gegen Erwarten stabil und bei 15 Torr ohne Zersetzung destillierbar ist.

Erhitzt man das Addukt mit Schwefel auf etwa 180°C, so wird zuerst Schwefelwasserstoff- und später Essigsäureentwicklung deutlich bemerkt. *o*-Diacetylbenzol müßte also in zwei Stufen entstanden sein. Aus dem Reaktionsgemisch wird eine schwach gelbe, klebrige Flüssigkeit mit demselben Siedepunkt wie *o*-Diacetylbenzol herausdestilliert. Diese Flüssigkeit, deren Elementaranalyse mit den für *o*-Diacetylbenzol berechneten gut übereinstimmt, zeigt sehr intensive violette Farbreaktion mit Anilin in essigsaurer Lösung in der Kälte und gibt ein Disemicarbazon, das beim Mischschmelzpunkt mit dem reinen *o*-Diacetylbenzol[5] keine Depression zeigt. Obgleich weitere Reinigung dieser Flüssigkeit sehr schwierig war, kristallisierte sie bei längegerem Stehen im Eisschrank—etwa über ein Jahr—zum Teil in schönen Nadeln, die nach einer Umkristallisation aus Petroläther einen Schmelzpunkt von 37°C zeigten[9]. Auch beim Erhitzen des Adduktes in der Luft unter normalem Druck bildete sich *o*-Diacetylbenzol, das als Disemicarbazon identifiziert werden konnte.

Chloranil und dessen Homologe werden oft als Aromatisierungsmittel empfohlen[10,11]. Wenn man das Addukt, 3-Acetoxy-1.2.3.6-tetrahydro-1.2-diacetylbenzol mit zwei molekularer Menge Chloranil in Xylol erhitzt, wird Essigsäureentwicklung beobachtet. Obwohl das Produkt auch starke Farbreaktion mit Anilin in essigsaurer Lösung zeigte und das erwartete *o*-Diacetylbenzol als Disemicarbazon identifiziert werden konnte, ließ es sich noch nicht genügend reinigen. Andere Versuche, z. B. Erwärmen mit Natriumhydrogencarbonat oder mit Selendioxyd, zerstörten die Substanz mehr oder weniger.



Ein Versuch zur Bromierung des Adduktes in der Allylstelle mit *N*-Bromsuccinimid in Tetrachlorkohlenstoff führte nur zur Harzbildung. Während sich beim Versetzen des Adduktes mit Brom in Tetrachlorkohlenstoff ein Harz unter Entwicklung des Bromwasserstoffs bildete—das Reaktionsgemisch zeigte jedoch mit Anilin violette Farbreaktion — wurde durch Versetzen mit Brom unter Zusatz von Pyridin eine kristallinische Dibromverbindung erhalten, die beim Aromatisieren unter Abspalten von Bromwasserstoff 3-Acetoxy-1.2-diacetylbenzol ergeben könne. Das aus der Dibromverbindung durch Erhitzen mit Pyridin hergestellte Produkt zeigte mit Anilin eine violette Farbreaktion und scheint nach Elementaranalyse ein noch unreines Präparat von 3-Acetoxy-1.2-diacetylbenzol zu sein.

6) A. Wacker, Ges. f. Elektrochem. Ind. GmbH., Engl. Pat., 463,196; *Chem. Zentr.*, **1939**, I, 796.
7) G. O. Schenk, *Ber.*, **77**, 661 (1944).
8) K. F. Armstrong und P. Robinson, *J. Chem. Soc.*, **1934**, 1650.
9) Vgl. die zu 3) angegebene Literatur, Fp. 38°C.
10) E. A. Braude, A. G. Brook und R. R. Linstead, *J. Chem. Soc.*, **1954**, 3569.
11) U. Eisner und R. R. Linstead, ebenda, **1955**, 3753.

Bemerkenswert ist, daß das Addukt selbst mit Anilin in essigsaurer Lösung beim Kochen eine intensive rote Farbreaktion zeigt. In der Kälte gibt es in verdünnter Essigsäure nach längerem Stehen mit Anilin eine rote Färbung, die sehr langsam in violette übergeht. Unter Erhitzen der Mischung findet die Veränderung der Farbe viel schneller statt als in der Kälte. Sowohl verschiedene Amine als auch Aminosäuren, die mit *o*-Diacetylbenzol eine violette Farbreaktion zeigen[5], reagierten auch mit dem Addukt zuerst unter einer Rotfärbung: die Farbe wurde beim Stehen langsam tiefer. Mit diesem Addukt konnten 10^{-4} bis 10^{-5} g primäre Amine auf Papierchromatogramme nachgewiesen werden. Zwar ist die Grenze des Nachweises praktisch gleicher Ordnung wie beim Nachweis mit *o*-Diacetylbenzol, es besteht aber der Nachteil des Adduktes als Nachweisreagens darin, daß für die Färbung längere Zeit benötigt wird. Der Nachteil ist jedoch nicht sehr entscheidend, weil das Addukt als *o*-Diacetylbenzol viel leichter und auch in viel größerem Maßstab hergestellt werden kann.

$\alpha.\beta$-Diacetyläthylen ergab Diels-Alder-Addukte weder mit Furan noch mit 2.3-Dimethoxybutadien-(1.3), soweit versucht wurde.

Beschreibung der Versuche

1. $\alpha.\beta$-Diacetyläthylen (I)[7,8].—Fp. 75.5～76.5°C (Lit.[8] 75.5～76.5°C) (aus Petroläther schwach gelbe Nadeln).

2. 1-Acetoxybutadien-(1.3)(II)[6].—$Kp._{30}$ 51～52°C.

3. 3-Acetoxy-1.2.3.6-tetrahydro-1.2-diacetylbenzol (III).—40 g I wurden in 300 ccm Äthanol mit 50 g II 24 Std. am Rückfluß in Abwesenheit von Feuchtigkeit gekocht, das Lösungsmittel im Vakuum abgedampft und der Rückstand im Vakuum zweimal fraktioniert, $Kp._{12}$ 156～159°C, Ausbeute 65 g (82%).

$C_{12}H_{16}O_4$ (224.2)

Ber. C 64.27 H 7.19
Gef. C 65.50 H 7.43

Diese Verbindung zeigt mit Anilin in essigsaurer Lösung in der Kälte eine rote Farbreaktion. Die Farbe wird langsam violett.

4. Versuch zur Aromatisierung von III zu *o*-Diacetylbenzol (IV).—(a) Mit Schwefel 25 g III wurden 5 Std. mit 3.5 g Schwefel bei 100 Torr auf 160～180°C erhitzt, wobei rege Schwefelwasserstoff- und Essigsäureentwicklung beobachtet wurden. Bei der Destillation des Reaktionsgemisches im Hochvakuum gingen 18 g schwach gelbes Öl bei 105°C und 0.05 Torr über.

$C_{10}H_{10}O_2$ (152.2) (*o*-Diacetylbenzol)

Ber. C 73.92 H 6.21
Gef. C 73.68 H 6.34

Dieses Öl zeigte eine intensive violette Farbreaktion mit Anilin-Essigsäure in der Kälte und kristallisierte zum Teil bei längerem Stehen im Eisschrank (über ein Jahr bei −5°C) in Nadeln, die aus Petroläther umkristallisiert wurden, Fp. 37°C (Lit.[3] 38°C), Ausbeute 2.3 g Disemicarbazon, Fp. 150°C (Lit.[3] 150°C).

(b) Mit Chloranil 4.5 g III wurden 40 Std. mit 9.4 g Chloranil in 500 ccm Xylol am Rückfluß erhitzt, wobei Essigsäureentwicklung beobachtet wurde. Das Reaktionsgemisch wurde abfiltriert, das Filtrat eingeengt und der Rückstand mit Petroläther ausgezogen. Die Petrolätherlösung zeigte eine intensive violette Farbreaktion mit Anilin-Essigsäure in der Kälte. Obgleich keine Kristalle von IV nach dem Abdampfen des Petroläthers erhalten wurden, konnte IV als Disemicarbazon (0.13 g) identifiziert werden.

(c) Mit der Luft 4.5 g III wurden 48 Std. auf ca. 150～160°C erhitzt. Obgleich der Petrolätherauszug des Reaktionsgemisches eine intensive violette Farbreaktion mit Anilin in essigsaurer Lösung zeigte und Disemicarbazon (0.25 g) von IV gibt, blieb der Versuch zur Reinigung des Produktes erfolglos.

(d) Mit Selendioxyd 1 g III wurde 1 Std. mit 200 mg Selendioxyd in 20 ccm Äthanol am Rückfluß erhitzt. Es wurde keine Farbreaktion mit Anilin mehr beobachtet.

(e) Mit Natriumhydrogencarbonat 450 mg III wurden 10 Min. mit 150 mg Natriumhydrogencarbonat in Äthanol-Wasser (1:1) erhitzt. Nach dem Ansäuern mit Essigsäure zeigte das Gemisch nur schwache violette Farbreaktion mit Anilin.

5. 3-Acetoxy-4.5-dibrom-1.2-diacetylcyclohexan (V).—1.6 g III wurden in 30 ccm Tetrachlorkohlenstoff mit Brom bei Raumtemperatur versetzt, wobei das Gemisch unter Bromwasserstoffentwicklung ein Harz bildet. Das Produkt zeigte jedoch mit Anilin in essigsaurer Lösung eine intensive Farbreaktion. Unter Zusatz von Pyridin und unter Eiskühlung findet aber beim Versetzen mit Brom Harzbildung kaum statt. Das Gemisch wurde nach Stehenlassen über Nacht abfiltriert, das Lösungsmittel im Vakuum abgedampft und der Rückstand aus Methanol umkristallisiert, farblose Nadeln, Ausbeute 0.9 g (35%), Fp. 90～92°C (Zers.).

$C_{12}H_{16}Br_2O_4$ (384.1)

Ber. C 37.52 H 4.20 Br 41.61
Gef. C 37.63 H 4.39 Br 42.60

6. Versuch zur Aromatisierung von V: 3-Acetoxy-1.2-diacetylbenzol.—2 g V wurden in 20 ccm Pyridin 20 Std. am Rückfluß erhitzt, das Lösungsmittel im Vakuum abgedampft, der harzige Rückstand mit Wasser gewaschen und im kleinen Destillationsapparat im Hochvakuum zweimal destilliert. Die schwach gelbe Flüssigkeit, die bei 130°C (Badetemperatur) und 0.05 Torr überging, war halogenfrei und zeigte mit Anilin in essigsaurer Lösung eine violette Farbreaktion, Ausbeute 0.05 g.

$C_{12}H_{12}O_4$ (220.2)

Ber. C 65.45 H 5.49
Gef. C 66.10 H 5.14

Das Produkt scheint ein noch unreines Präparat von 3-Acetoxy-1.2-diacetylbenzol, zu sein konnte

jedoch wegen sehr schlechter Ausbeute nicht mehr gereinigt werden.

Zusammenfassung

1-Acetoxybutadien-(1.3) gibt mit $\alpha.\beta$-Diacetyläthylen das Addukt: 1-Acetoxy-1.2.3.6-tetrahydro-1.2-diacetylbenzol, das durch Schwefel zu *o*-Diacetylbenzol aromatisiert werden konnte. Die Synthese ist in großem Maßstab leicht durchzuführen. Das Addukt reagiert mit primären Aminen unter einer roten Färbung und die Farbe geht langsam in violette über. Es wurden noch Reaktionen des Adduktes mit Brom untersucht.

Herrn Prof. Dr. F. Weygand, München, sage ich an dieser Stelle meinen aufrichtigsten Dank für Anregung und Anleitung zu vorstehender Arbeit.

Organisch-Chemisches Laboratorium der Technischen Hochschule Nagoya Syôwa-ku, Nagoya

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Studies on Arsenic Trisulfide Glass

By Jiro MATSUDA

(Received August 11, 1959)

The arsenic trisulfide glass has been studied as one of the new optical materials, because it can transmit infrared rays very well and has marked resistance to water and acid, and is more easily manufactured than single crystals[1-5].

The author once studied some different methods of preparation for technical arsenic trisulfide glass, and found the transmission value to be about 70% between 2 and 12 μ for 1 mm. thickness[6]. This figure is the maximum of the transmission value of this glass and the rather low transparency in this case results from the surface reflection and high refractive index[7]. If this glass can be properly coated on the surface, it will be more suitable for optical purposes, for this process must assist in reducing the reflection at the surface and raising the poor resistance to alkali.

Apart from the question of optical materials, the arsenic trisulfide glass is the interesting experimental glass composed of one component which melts at low temperature (about 300°C). Since the publication of the theory by Zachariasen[8] and the introduction of the X-ray analysis by Warren[9], glassy substances are explained as homogeneous polymers which characterize the amorphous substances consisting of network formers and modifiers, but some writers have insisted that glass is composed of a microheterogeneous system by microcrystalline structure[10]. These different views are closely related to the process of the transition of solids[11]. What process of transition occurs in glassy substances? The solution of this problem is very interesting and necessary in investigating the structure of glass. The various physical properties have frequently been studied on this point. The color of arsenic trisulfide has been found to be remarkably sensitive to changes in temperature. When it is heated yellow arsenic trisulfide is transformed to red and then to black. At 100°C, red aesenic trisulfide and at 170°C black substances can be obtained[12,13].

The author studied the thermal expansion values of red arsenic trisulfide glass

1) R. Frerichs, *Phys. Rev.*, **78**, 643 (1950).
2) W. A. Fraser, *J. Opt. Soc. Am.*, **43**, 322 (1953).
3) W. A. Fraser, ibid., **43**, 823 (1953).
4) R. Frerichs, ibid., **43**, 1153 (1953).
5) M. H. Bloch, *J. Research Natl. Bur. Standards*, **59**, 2774 (1957).
6) Presented before the Annual Conference on the Artificial Minerals, Nagoya, October, 1958. This result was published in *the Review of Physical Chemistry of Japan*, **29**, 22 (1959).
7) 2.43 at 5μ.
8) W. H. Zachariasen, *J. Am. Chem. Soc.*, **54**, 3841 (1932).
9) B. E. Warren et al., *J. Am. Ceram. Soc.*, **21**, 49 (1935).
10) For example, K. S. Evstropyev, "The Structure of Glass", Consultants Bureau, Inc., New York (1958), p. 9.
11) F. C. Kracer, "Phase Transformations in Solids", John Wiley & Sons, Inc., New York (1951), p. 257.
12) H. Winter, *Z. anorg. u. allgem. Chem.*, **34**, 228 (1904).
13) E. W. Blank, *J. Chem. Educ.*, **20**, 171 (1943).

at transition temperatures by the quenching method and investigated the process of the transition.

Experimental

The preparation of techincal arsenic trisulfide, the casting and the polishing of the glass were done by the same methods as mentioned in the previous report (Ref. 6).

Terylene film was used to coat the surface of the glass, because it can form the transparent, thin and filmy state easily at fairly low temperature and has a proper refractive index to remove the surface loss peculiar to the arsenic trisulfide glass. Terylene was dissolved in *o*-chlorophenol and this dilute solution was dropped on the glass which was horizontally rotated by an electric motor. Such treated glass was dried at 80°C in an air bath. The chemical durability of the glass to alkali was measured by spectroscopic method; that is, some pieces of glass were experimentally dipped in aqueous solution of sodium hydroxide for a limited time. After such etching they were washed and dried and measured on the falling of the transmittance at 2 μ wavelength.

The thermal expansion was measured by the ordinary optical lever method. Throughout the measuring, the samples were heated in succession at the constant rate of 2°C a minute. Before heating they were annealed at the constant temperature (187°C) for three days and allowed to cool very slowly to room temperature about 60 hr. in the electric annealing oven. They were then reheated for several hours at various temperatures ranging from 153 to 180°C and were quenched in the air.

The heating was made always in an mobile oil bath to prevent arsenic trisulfide from oxidizing.

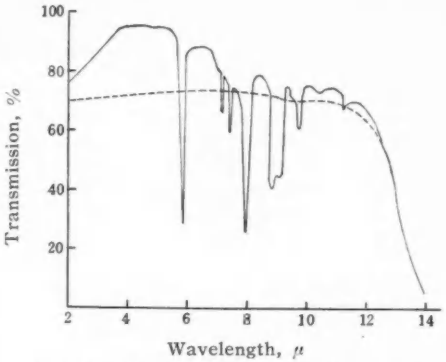

Fig. 1. Effect of coating on the arsenic trisulfide glass of 1 mm. thickness.
——: coated.
----: not coated.

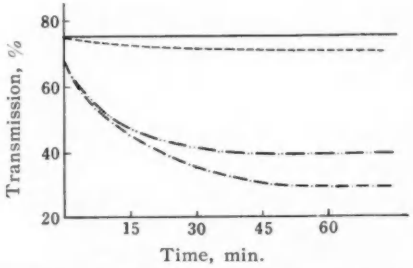

Fig. 2. Transmission after treatment in alkali.
—— and ----: coated glass treated in 0.05 and 0.1 N, respectively.
·—·—· and ·—·—·: uncoated glass treated in 0.05 and 0.1 N, respectively.

Results and Discussion

Coating of the Surface. — As shown in Fig. 1, the effect of the coating is very remarkable in the range of short wavelengths, while it gradually decreases in the wavelengths which are over 7 μ and many absorption bands of surface film appear. If the film coated on the surface is so thin that interference color can be seen, the efficacy of the treatment in the rays of the short wavelengths is very conspicuous. In that case the transmittance is 75 to 95% between 2 and 5.7 μ. Moreover, even such a thin film markedly increases durability to alkali. As shown in Fig. 2, when dipped in 0.05 N alkaline solution, the coated glass is hardly affected at all. After 15 hr. etching the transmittance decreases by about only 4%.

In the case of 0.1 N, the coated glass is affected in some degree, but even after dipping for 30 min. the transmittance decreases by only 1~2%. All these decreases of the transmission were observed to be caused by etching pits which grew up from mechanical scratches on the film. These results mean that terylene film has sufficient protecting action against alkaline etching in such concentrations. As these results show, such coated arsenic trisulfide glass is of good use as optical material of the cell in the infrared between 2 and 5.7 μ and as seen in Fig. 1, the uncoated glass can be utilized as basic glass to study infrared absorption of various substances. Besides the terylene film, by proper coating of other materials the arsenic trisulfide glass seems to be the more valuable optical material.

Thermal Expansion. — The physical properties of glass are affected remarkably by different thermal histories. The abnormal thermal expansion of borosilicate

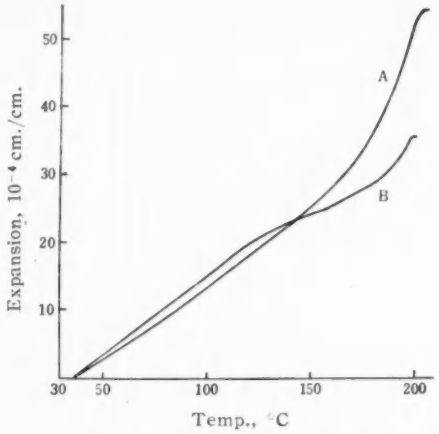

Fig. 3. Thermal expansion.
A: annealed, B: chilled.

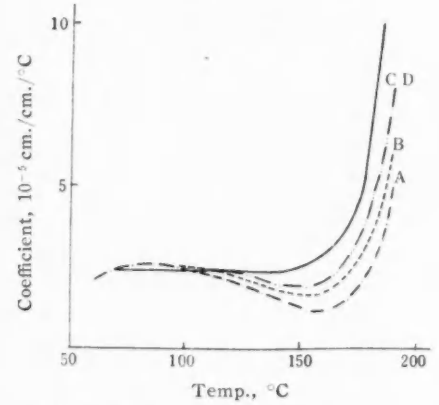

Fig. 4. Different coefficients among annealed and chilled glass.
——: annealed glass.
A, B, C and D are quenched at 180, 174, 164, and 153°C, respectively.

glass is one of the well-known examples of these sorts. As shown in Fig. 3, the annealed arsenic trisulfide glass shows transformation point at 170°C. The meaning of the transformation point in glass is not always the same in crystallography, but it is an undoubted fact that the structure of glass may change to a certain extent near the point. On the other hand, the precipitated arsenic trisulfide is said to have transformation points near 100 and 170°C[12-14]. However, in the case of the glassy state, the transformation appeared only at 170°C. Accordingly in order to study the common transformation point of these different solid states, the various coefficients of expansion were measured by the quenching method. A, B, C and D shown in Fig. 4. represent respectively the quenched specimens at 180, 174, 164 and 153°C. In Fig. 4, both A and B indicate larger values of the coefficients than in annealed glass below 100°C, but C and D almost the same values as annealed glass; that is, the quenching effect does not appear in the case of C and D.

In the high temperature range, the higher the quenching temperature becomes, the smaller the coefficient becomes, arriving at the minimum value near 160°C, but no substantial difference can be found among A, B, C and D curves and these results suggest that there is no intrinsic difference among the internal structures of the four specimens; that is, the difference of the coefficients shows the extent of their polymerization, and the higher the quenching temperature becomes, the more insufficient the polymerization becomes. This fact is guessed also from the difference among their exact temperatures at which the graduation of the dilatometer begins to show shrinking.

TABLE I. QUENCHING EFFECT ON THE EXACT TEMPERATURE AT WHICH THE ELONGATION CURVE ON THE DILATOMETER BEGINS TO SHOW SHRINKING

Sample	Temp., °C
A	200
B	200
C	202
D	206
annealed	209

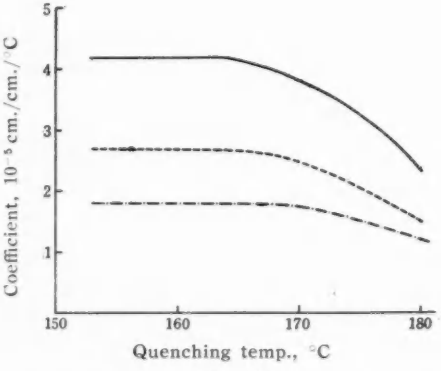

Fig. 5
——, ----, and —·—: measured at 180, 170 and 160°C, respectively.

14) W. A. Jonker, *Z. anorg. u. allgem. Chem.*, **62** 89, (1909).

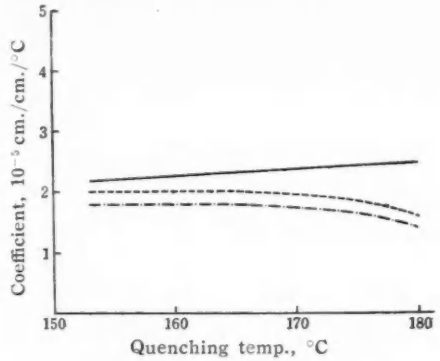

Fig. 6

——, ----, and —·—: measured at 100, 140 and 150°C, respectively.

These results are given in the table. As can been seen, the higher the quenching temperature becomes, the lower the exact temperature becomes; that is, the less sufficient the polymerization becomes.

Figs. 5 and 6 show the interrelation between the quenching temperature and the temperature in measuring of the coefficients. The abscissa means the quenching temperature. The differences among four specimens are notable at 180°C of measuring-temperature and become smaller at low temperature and at 100°C almost disappear. In all specimens the coefficients measured above 160°C, increase as the temperature rises, but this phenomenon appears in reverse below 150°C. Consequently all specimens show the minimum coefficient between 150 and 160°C. However, while the quenching temperature rises, the coefficients decrease in all cases above 100°C.

Summary

Arsenic trisulfide glass shows 70% of transmittance between 2 and 12 μ. This transmittance is somewhat insufficient for the optical cell in the infrared. Moreover, the chemical durability to alkali is very weak. These defects can be removed by proper coating on the surface. For instance, it can be of good use between 2 and 5.7 μ by using terylene film.

In thermal expansion, the transformation point of glassy arsenic trisulfide is nearly 170°C. In order to study what process of transformation occurs in the glass, the quenching method was applied. Some pieces of annealed glass were experimentally quenched at 180, 174, 164 and 153°C. Thermal expansion was measured on these quenched glasses.

Because of their various controls of expansion by temperature, glassy transformation at 170°C has no connection with transformation at the same temperature in arsenic trisulfide.

The author wishes to express his thanks to Mr. S. Matsuzaki for valuable cooperation and to Maruzen Oil Co., Ltd. for their kindness in the measuring of transmittance in the infrared.

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Surface Tension and Spinnability of Molten Poly-ε-capramide

By Naoya OGATA

(Received August 13, 1959)

Surface tension of a liquid means the tension in the boundary between a liquid and a gas or the free energy of the surface. As surface tension tends to make the area of surface as small as possible, it is expected that the spinnability of a liquid would have relation with its surface tension and hence physical properties concerning its surface can be estimated. Surface tension of molten ε-caprolactam and poly-ε-capramide has been measured and their surface properties have been studied.

Experimental

Polymerization of ε-Caprolactam. — ε-Caprolactam was polymerized at 257°C for 15 hr. in the presence of 5% of ε-aminocaproic acid and 2, 1 or 0.5 mol. % of benzoic acid. The degree of polymerization of polymers was estimated from the solution viscosity in *m*-cresol at 25°C by the following equation[1].

$$\overline{P}=127[\eta]^{1.435} \quad (1)$$

Measurement of Surface Tension. — Surface tension of molten ε-caprolactam or poly-ε-capramide was measured by the method of maximum bubble pressure[2]. When a capillary is immersed in a liquid and gas pressure is raised slowly, a bubble is formed at the tip of the capillary. If gas pressure is further raised, the bubble breaks away from the tip and the pressure decreases. Hence, the pressure passes through a maximum. When the main radius of curvature at the largest bubble is R and the depth of the tip of the capillary is h, the maximum pressure is given by the following equation.

$$P=2\gamma/R+Dgh \quad (2)$$

where γ, g and D mean surface tension, gravity constant and density, respectively. If the radius of a capillary is narrow enough, R can be approximated to the capillary radius r.

The tip of the capillary of 0.02~0.05 cm. radius was immersed in the melted substance at 1 cm. in depth and nitrogen gas was introduced slowly at the pressure rate of 0.1 cm. H_2O/min. and the maximum bubble pressure was measured.

Measurement of Spinnability.—The apparatus is shown in Fig. 1. A glass stick of radius of 0.2 cm. was immersed in molten poly-ε-capramide at 0.5 cm. in depth and was pulled up at the constant rate. The clutch was cut off immediately at the break of the thread and the length was measured.

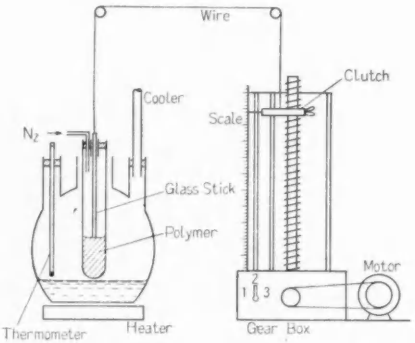

Fig. 1. Apparatus for the measurement of spinnability of poly-ε-capramide.

Results

Surface Tension of Molten ε-Caprolactam and Poly-ε-capramide. — Surface tension values of molten ε-caprolactam and *N*-acetyl-ε-aminocaproic acid to nitrogen gas at various temperatues are shown in Fig. 2.

Surface tension values of poly-ε-capramide of various polymerization degrees and at various temperatures are shown in Figs. 3 and 4. The poly-ε-capramide

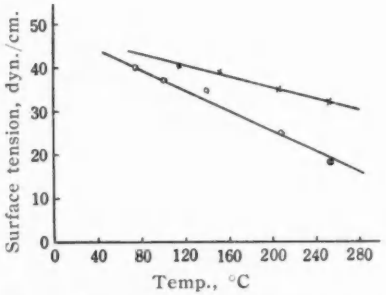

Fig. 2. Surface tension of ε-caprolactam and *N*-acetyl-ε-aminocaproic acid at various temperatures.
× *N*-Acetyl-ε-caprolactam
○ ε-Caprolactam

1) O. Fukumoto, *J. Polymer Sci.*, **22**, 263 (1956).
2) J. J. Bikerman, "Surface Tension", 2nd Ed., Academic Press, Inc., New York (1948), p. 17.

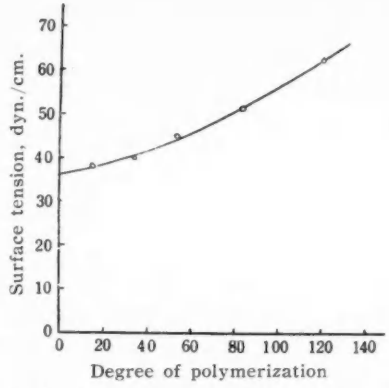

Fig. 3. Surface tension of poly-ε-capramide.

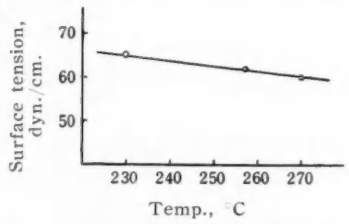

Fig. 4. Surface tension of poly-ε-capramide ($\bar{P}_n$=120) at various temperatures.

used was an equilibrium polymer containing about 10% of ε-caprolactam and its oligomers.

Thread Length of Poly-ε-capramide.—The thread lengths of poly-ε-capramide of various polymerization degrees at 230 or 257°C and at various pulling rates are shown in Fig. 5. The thread length of poly-ε-capramide ($\bar{P}$=120) at 257°C and at the pulling rate of 0.74 cm./sec. is proportional to the radius of a glass stick as shown in Fig. 6. Each polymer contained about 10% of ε-caprolactam and its oligomers.

Discussion

Ramsay and Shields[3] found a linear relation between surface tension of a liquid and temperature as the following equation:

$$\gamma(M/D)^{2/3}=k(T_c-T-6) \qquad (3)$$

where γ is surface tension, M is molecular weight, D is density, T_c is critical temperature and k is a constant characteristic for a liquid.

3) W. Ramsay and J. Shields, *Z. physik. Chem.*, **12**, 433 (1893).

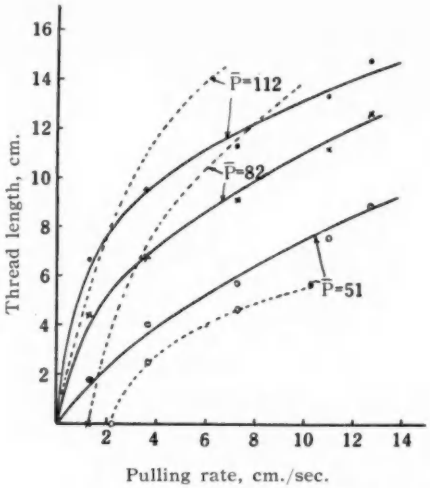

Fig. 5. Thread length at various pulling rates.
—— 230°C, ------ 257°C.

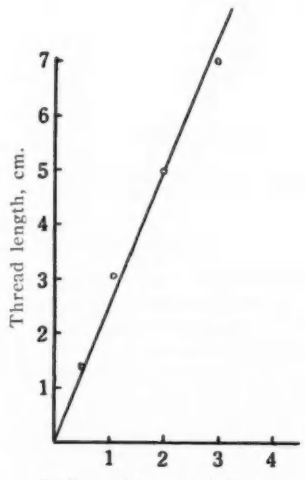

Fig. 6. The relation between thread length and radius of glass stick.
($\bar{P}$=120, V=0.74 cm./sec., t=257°C)

The value of k for a normal liquid is usually about 2.12. The value of k and the critical temperature of ε-caprolactam is estimated to be 2.77 and 463°C, respectively.

Surface tension of poly-ε-capramide increases as the degree of polymerization increases. When the logarithms of surface-tension γ are plotted against the polymerization degree $\bar{P}$, a linear relation is

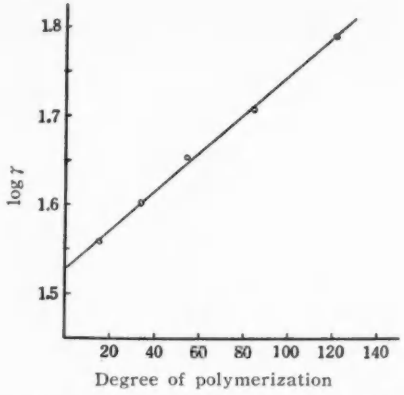

Fig. 7. Relation between $\log\gamma$ and $\bar{P}$.

obtained as shown in Fig. 7 and the following equation is obtained at 257°C.

$$\log\gamma = 0.0022\bar{P} + 1.53 \quad (5)$$

As the surface tension of poly-ε-capramide ($\bar{P}=120$) is nearly proportional to temperature from Fig. 4, the value of $d\gamma/dT$ is about -0.06 dyn./cm. deg. and that of *N*-acetyl-ε-aminocaproic acid is also -0.06 dyn./cm. deg. Therefore, the value of $d\gamma/dT$ of linear poly-ε-capramide is expected to be -0.06 dyn./cm. deg. independent of the polymerization degree, and the following equation is obtained, where t is temperature in degrees centigrade.

$$\gamma = 10^{(0.0022\bar{P}+1.53)} + 0.06(257-t) \quad (6)$$

Surface tension of ε-aminocaproic acid at 252°C is estimated from Eq. 6 to be about 34 dyn./cm. This value is not consistent with the surface tension value of ε-caprolactam (18 dyn./cm.), but is nearly approximated to that of *N*-acetyl-ε-aminocaproic acid (32 dyn./cm.). Therefore, it is expected that the surface tension of ε-aminocaproic acid is about 16 dyn./cm. greater than that of ε-caprolactam.

Since surface tension means intermolecular forces among molecules, this result suggests that the intermolecular force of ε-aminocaproic acid is greater than that of ε-caprolactam.

The total surface energy U is given[2] by

$$U = \gamma - T\partial\gamma/\partial T \quad (7)$$

The total surface energies of ε-caprolactam, *N*-acetyl-ε-aminocaproic acid and poly-ε-capramide are shown in Tables I and II.

The total surface energy of ε-aminocaproic acid is estimated to be about 66

TABLE I. TOTAL SURFACE ENERGY OF ε-CAPROLACTAM, *N*-ACETYL-ε-AMINOCAPROIC ACID AND POLY-ε-CAPRAMIDE

Sample	Temp. °C	γ(dyn./cm.)	$\partial\gamma/\partial T$	U(erg/cm²)
ε-Caprolactam	76	40	−0.12	82
	100	37	−0.12	82
	140	35	−0.12	85
	208	25	−0.12	83
	252	18	−0.12	81
Mean value	—	—	−0.12	82
N-Acetyl-ε-aminocaproic acid	116	40	−0.06	63
	152	39	−0.06	65
	205	35	−0.06	64
	252	32	−0.06	64
Mean value	—	—	−0.06	64
Poly-ε-capramide ($\bar{P}$=120)	230	65	−0.06	95
	257	62	−0.06	94
	270	60	−0.06	93
Mean value	—	—	−0.06	94

TABLE II. TOTAL SURFACE ENERGY OF POLY-ε-CAPRAMIDE

$\bar{P}$	γ(dyn./cm.)	U(erg/cm²)
15	38	70
34	40	72
54	45	77
84	51	83
121	62	94

erg/cm² from Table I and is 16 erg/cm² smaller than that of ε-caprolactam. This result is very interesting in relation to the exothermic reaction of the ε-caprolactam polymerization[4,5].

It is presumed that the increase in surface tension of poly-ε-capramide with the increase of its polymerization degree may be caused by the difference in thermal movement of macromolecules.

It is assumed that the thread of molten poly-ε-capramide may be broken at the point at which the surface energy reaches equilibrium with the friction energy of viscous liquid. Hirai[6] introduced the following equation in relation to surface tension γ and thread length L, and ascertained this equation for the thread length of glycerine.

$$L = R_0 V\mu/\gamma \quad (8)$$

4) S. M. Skuratov et al., *Kolloid Zhur.*, **14**, 185 (1952); *Faserforsch. u. Textiltech.*, **4**, 390 (1953).
5) H. Yumoto, This Bulletin, **28**, 94 (1955).
6) N. Hirai, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **75**, 1019 (1954); *Chem. Abstr.*, **46**, 9357*h* (1955).

In this equation R_0 is the radius of a glass stick, μ is the viscosity and V is the pulling rate. In case of poly-ε-capramide, L is not proportional to V as shown in Fig. 5. However, a linear relation is obtained by plotting $\log L$ against $\log V$, as shown in Fig. 8.

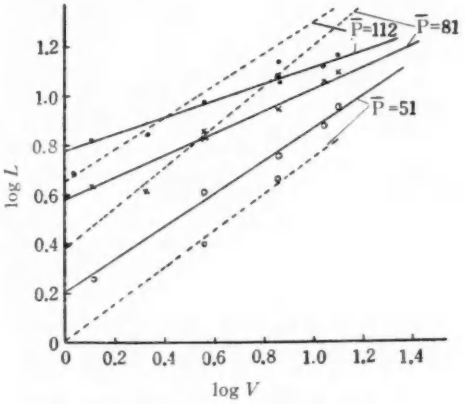

Fig. 8. Relation between $\log L$ and $\log V$.
—— 230°C, ------ 257°C.

Since L was proportional to the radius R_0 of a glass stick, the following equation is given:

$$L = kR_0V^a \tag{9}$$

The values of k and a at various polymerization degrees and temperatures are shown in Table III, where R_0 and V are given in cm. and cm./sec. units, respectively.

TABLE III. THE VALUES OF k AND a IN $L = kR_0V^a$

Temp., °C	$\bar{P}$	k	a
230	51	8	0.6
	82	16	0.4
	112	30	0.4
257	51	5	0.7
	82	12	0.7
	112	23	0.6

The value of a is almost invariable and its mean value is 0.5. Therefore, the thread length is proportional to the square root of the pulling rate.

The values of μ/γ, which are shown in Table IV, were estimated from the following equation derived by K. Hoshino[7].

$$\log \mu = -7 + 2300/T + 6.2([\eta]^{25°C}_{\text{cresol}})^{1/2} \tag{10}$$

7) K. Hoshino and S. Fujii, *Chem. High Polymers (Kobunshi Kagaku)*, **1**, 14 (1944); *Chem. Abstr.*, **44**, 5147b (1950).

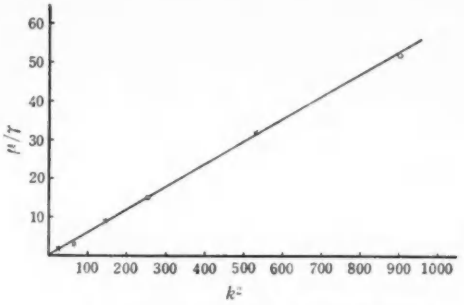

Fig. 9. The relation between k^2 and μ/γ.

TABLE IV. THE VALUE OF μ/γ

Temp. °C	$\bar{P}$	$[\eta]^{25°C}_{\text{cresol}}$	μ (poise)	μ/γ	k^2
230	51	0.53	123	3	64
	82	0.74	810	15	256
	112	0.92	3240	52	900
257	51	0.53	73	2	25
	82	0.74	480	9	144
	112	0.92	1900	32	529

When the value of k^2 is plotted against μ/γ, a linear relation is obtained as shown in Fig. 9 and the following equation is given.

$$\mu/\gamma = 0.059k^2 \tag{11}$$

From Eqs. 9 and 11, the thread length of poly-ε-capramide can be represented as follows:

$$L = 4.13R_0(\mu V/\gamma)^{1/2} \tag{12}$$

It can be estimated from the above-mentioned results that the thread length of molten poly-ε-capramide of $\bar{P} = 100 \sim 120$ at 257°C may be approximately 12 cm., when the polymer is spun at the rate of 400 m./min. from a nozzle of 0.02 cm. radius, and the fiber must be cooled within this length to obtain a continuous filament.

Summary

Surface tension of molten ε-caprolactam and poly-ε-capramide has been measured by the method of maximum bubble pressure. Surface tension of ε-caprolactam at 252°C is 18 dyn./cm. and it is 16 dyn./cm. smaller than that of ε-aminocaproic acid (34 dyn./cm.). It is estimated from the Ramsay-Shields' equation that the critical temperature of ε-caprolactam is 463°C. Surface tension of poly-ε-capramide of the polymerization degree $\bar{P}$ is given by the following equation.

$$\gamma = 10^{(0.0022\bar{P}+1.53)} + 0.06(257 - t)$$

The thread length of molten poly-ε-capramide has been measured by pulling up a glass stick and is represented by the following equation, where L (cm.) is thread length, R_0 (cm.) radius of a glass stick, μ (poise) melt viscosity, γ (dyn./cm.) surface tension and V (cm./sec.) pulling rate:

$$L = 4.13R_0(\mu V/\gamma)^{1/2}$$

The author wishes to thank Dr. K. Hoshino and Dr. H. Kobayashi who instructed him in this study and permitted the publication of these results. He also thanks Mr. M. Nakata who collaborated with him in experiments.

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Phase Equilibrium on Liquidus Surface of the System $3CaO \cdot P_2O_5$-$CaO \cdot MgO \cdot 2SiO_2$-$MgO \cdot SiO_2$

By Toshiyuki SATA

(Received August 15, 1959)

As a continuation of the author's preceding reports, which were on the phase relationship in the systems $3CaO \cdot P_2O_5$-$MgO \cdot SiO_2$-SiO_2[1] and $3CaO \cdot P_2O_5$-$CaO \cdot MgO \cdot 2SiO_2$-$SiO_2$[2], an equilibrium study on the system $3CaO \cdot P_2O_5$-$CaO \cdot MgO \cdot 2SiO_2$-$MgO \cdot SiO_2$, a side plane of a tetrahedron of a system $3CaO \cdot P_2O_5$-$CaO \cdot MgO \cdot 2SiO_2$-$MgO \cdot SiO_2$-$SiO_2$, was carried out by the usual quenching method. On the phase relationship of this 3-component system, no paper has ever been presented.

Of the three component system concerned, data of the two partial systems, $3CaO \cdot P_2O_5$-$CaO \cdot MgO \cdot 2SiO_2$ and $3CaO \cdot P_2O_5$-$MgO \cdot SiO_2$, were already given by the author's reports. Another partial system $CaO \cdot MgO \cdot 2SiO_2$-$MgO \cdot SiO_2$ was investigated by Bowen[3]. In his phase diagram, it is characterized that forsterite is a primary phase at 22~100% of $MgO \cdot SiO_2$. However, in the phase diagram published in 1952 by Atlas[4], who studied the matter by adding LiF, the primary phase may be a solid solution at overall range, which is decomposed to a clinoenstatite, diopside, protoenstatite or rhombic enstatite solid solution in a crystalline phase. In this report the author followed Bowen's diagram, and constructed the phase diagram on the liquidus surface of this system.

1) T. Sata, This Bulletin, **31**, 408 (1958).
2) T. Sata, ibid, **32**, 105 (1959).
3) N. L. Bowen, *Z. anorg. u. allgem. Chem.*, **90**, 1—66 (1914).
4) L. Atlas, *J. Geology*, **60**, 140 (1952).

Experimental

The nine compositions taken on the system $CaO \cdot MgO \cdot 2SiO_2$-$MgO \cdot SiO_2$ are listed in Table I. Then on the line joining these nine compositions with $3CaO \cdot P_2O_5$ point, thirty-two sample points were taken in the system $3CaO \cdot P_2O_5$-$CaO \cdot MgO \cdot 2SiO_2$-$MgO \cdot SiO_2$ and plotted in Fig. 1.

Powdered batches of these compositions, prepared by quenching into a glass after being kept at above their melting points, were again held at constant temperatures in a silicon carbide resister furnace and then quenched in water. Thenceforth the equilibrium phases found therein were determined by optical and X-ray examination. For measuring the temperature a thermocouple of platinum-platinum rhodium (10%) was used. Details of the experimental procedures are similar to those already described in the preceding report[1].

TABLE I. COMPOSITIONS OF SAMPLES TAKEN FROM THE SYSTEM $CaO \cdot MgO \cdot 2SiO_2$-$MgO \cdot SiO_2$

No.	$CaO \cdot MgO \cdot 2SiO_2$	$MgO \cdot SiO_2$
	wt. %	
225	85	15
240	80	20
—	75	25
209	70	30
230	60	40
210	50	50
238	40	60
211	20	80

Results

Data on the quenching runs for this 3-component system are listed in Table II,

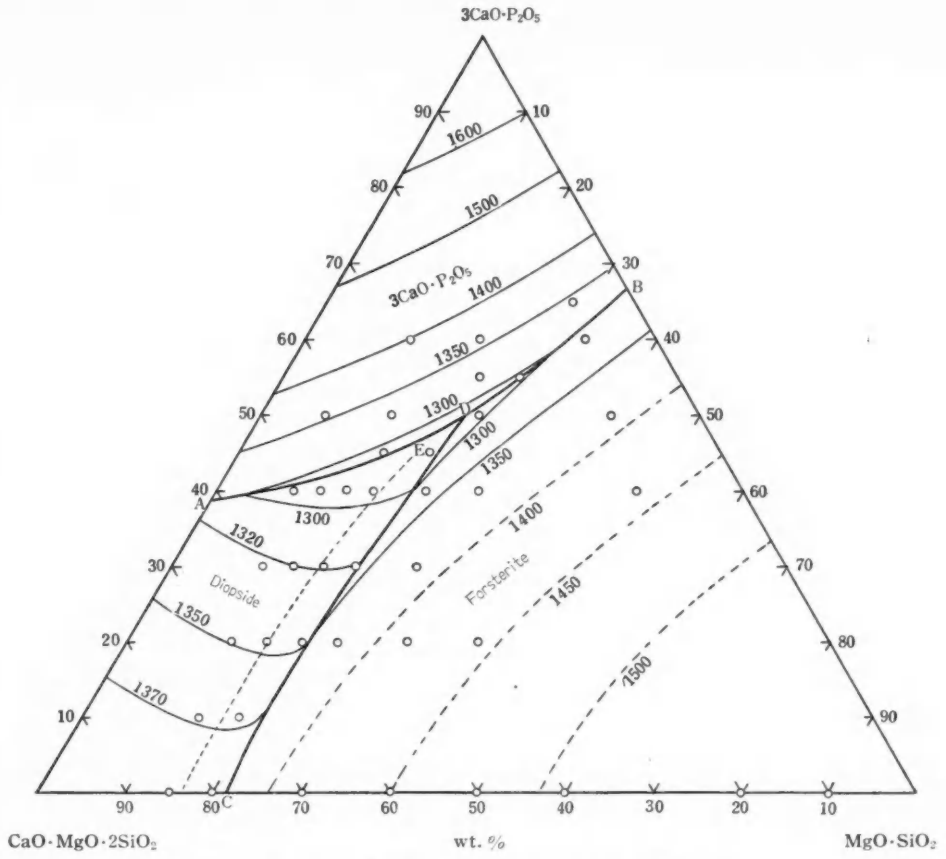

Fig. 1. The system $3CaO \cdot P_2O_5$–$CaO \cdot MgO \cdot 2SiO_2$–$MgO \cdot SiO_2$.
(A: 1314°C, B: 1308°C, C: 1390°C)

from which the equilibrium diagram on the liquidus surface was constructed as shown in Fig. 1. Primary crystals in this system are tricalcium phosphate (α or β), diopside and forsterite, respectively, and forsterite occupies a wide field. Accordingly it is found that this system is not a ternary one.

A lower liquidus temperature range is located in the center of this triangle, its minimum temperature being 1277±5°C. A temperature minimum at 1389°C in the system $CaO \cdot MgO \cdot 2SiO_2$–$MgO \cdot SiO_2$ falls slowly toward the neighborhood of this lowest point as shown by a dotted line. However, it can not be decided in this report whether this valley of temperature attains to this point or not. Clinoenstatite does not appear as a primary crystal on the liquidus surface. Hence a decomposition of pyroxene solid solution to colinoenstatite may occur under the liquidus.

Summary

The phase relationship on the liquidus surface of the system $3CaO \cdot P_2O_5$–$CaO \cdot MgO \cdot 2SiO_2$–$MgO \cdot SiO_2$ was investigated by the usual quenching method. The three primary crystals are α- or β-tricalcium phosphate, diopside and forsterite, and the range of the lowest temperature is located at the center of this triangle (1277°C). From these results, it is found that this system should be considered as a partial system in the 4-component system $3CaO \cdot P_2O_5$–$CaO \cdot MgO \cdot 2SiO_2$–$2MgO \cdot SiO_2$–$SiO_2$.

TABLE II. QUENCHING DATA IN THE SYSTEM $3CaO \cdot P_2O_5$-$CaO \cdot MgO \cdot 2SiO_2$-$MgO \cdot SiO_2$

No.	Composition wt. %		C_3P	CMS_2 wt. %	MS*	Holding temp. °C	time min.	Phases present
	C_3P No. 225							
226	50	50	50	42.5	7.5	1347	30	gl.*
						1340	30	β-C_3P, gl.
227	40	60	40	51.0	9.0	1307	30	gl.
						1298	30	faint diopside, gl.
						1290	40	diopside, gl.
						1282	40	all crystal
228	30	70	30	59.5	10.5	1332	60	gl.
						1325	30	small diopside, gl.
						1290	30	diopside, gl.
						1282	30	all crystal
235	20	80	20	68.0	12.0	1356	30	gl.
						1347	30	faint diopside, gl.
236	10	90	10	76.5	13.5	1372	30	gl.
						1364	30	diopside, gl.
						1340	30	diopside, small gl.
	C_3P No. 240							
241	40	60	40	48	12	1307	30	faint diopside, gl.
						1290	30	diopside, gl.
242	30	70	30	56	14	1332	60	gl.
						1325	30	small diopside, gl.
						1307	30	diopside, gl.
243	20	80	20	64	16	1356	20	gl.
						1347	30	small diopside, gl.
244	10	90	10	72	18	1372	30	gl.
						1364	30	diopside, gl.
245**			40	45	15	1302	30	small diopside, gl.
						1294	30	diopside, gl.
						1286	30	diopside, gl.
246**			30	52.5	17.5	1314	40	gl.
						1307	40	diopside, gl.
247**			20	60	20	1357	50	gl.
						1347	30	faint diopside, gl.
	C_3P No. 209							
212	60	40	60	28	12	1356	40	gl.
						1348	40	β-C_3P, gl.
						1282	40	β-C_3P, gl.
213	50	50	50	35	15	1330	40	gl.
						1307	40	small C_3P, gl.
						1282	40	β-C_3P, gl.
						1273	30	all crystal
221	45	55	45	38.5	16.5	1307	30	gl.
						1282	30	small C_3P, gl.
						1274	50	all crystal
214	40	60	40	42	18	1302	30	gl.
						1294	30	faint diopside, gl.
						1286	30	small diopside, gl.
						1273	30	all crystal

* Abbreviations: $C_3P = 3CaO \cdot P_2O_5$; $CMS_2 = CaO \cdot MgO \cdot 2SiO_2$; $MS = MgO \cdot SiO_2$; gl. = glass.

** No. 245, 246, 247 were prepared from 1 : 1 mixture of No. 241—No. 214, No. 242—No. 222, No. 243—No. 229, respectively.

222	30	70	30	49	21	1324	40	gl.
						1314	40	faint diopside, gl.
						1282	40	diopside, small gl.
229	20	80	20	56	24	1407	30	gl.
						1397	40	small forsterite, gl.
						1340	50	forsterite, gl.
						1332	60	forsterite, diopside, gl.
						1322	60	forsterite, diopside, gl.
	C_3P No. 230							
231	45	55	45	33	22	1290	30	gl.
						1282	30	small diopside, gl.
						1272	30	diopside, β-C_3P, gl.
						1265	30	all crystal
232	40	60	40	36	24	1323	60	gl.
						1314	60	small forsterite, gl.
						1299	60	forsterite, gl.
						1290	40	forsterite, diopside, gl.
233	30	70	30	42	28	1397	40	gl.
						1390	30	small forsterite, gl.
						1323	30	forsterite, gl.
						1314	60	forsterite, small diopside, gl.
						1250	60	forsterite, diopside, β-C_3P
234	20	80	20	48	32	1460	30	gl.
						1450	30	small forsterite, gl.
	C_3P No. 210							
215	60	40	60	20	20	1348	40	gl.
						1340	40	very small C_3P, gl.
						1332	40	small C_3P, gl.
223	55	45	55	22.5	22.5	1314	40	gl.
						1307	30	small C_3P, gl.
216	50	50	50	25	25	1298	30	gl.
						1290	30	faint forsterite, gl.
						1282	20	forsterite, gl.
						1277	30	forsterite, C_3P, gl.
217	40	60	40	30	30	1365	50	gl.
						1356	40	small forsterite, gl.
237	20	80	20	40	40	1499	15	gl.
						1480	20	small forsterite, gl.
	C_3P No. 238							
239	55	45	55	18	27	1297	30	faint C_3P, forsterite, gl.
						1290	30	C_3P, forsterite, gl.
	C_3P No. 211							
224	65	35	65	28	7	1340	30	gl.
						1332	40	small C_3P, gl.
						1299	30	β-C_3P, gl.
						1290	30	β-C_3P, forsterite, gl.
218	60	40	60	32	8	1314	40	gl.
						1307	50	small forsterite, C_3P, gl.
219	50	50	50	40	10	1422	30	gl.
						1407	30	small forsterite, gl.
						1365	50	forsterite gl.
						1250	60	forsterite, β-C_3P, diopside
220	40	60	40	48	12	1479	15	gl.
						1460	20	small forsterite, gl.
						1432	20	forsterite, gl.

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Ultraviolet Absorption Spectra of o-, m- and p-Dinitrobenzene

By Takehiro ABE

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Introduction of a substituent group for hydrogen in a benzene nucleus has been considered to shift in general the spectrum of the original benzene derivative to longer wavelengths. In the previous papers[1,2], however, the author found that absorption maximum bands of *m*-dinitrobenzene, 1,3,5-trinitrobenzene and 2,4,6-trinitrotoluene shifted to the blue as compared with the intense 260 mμ band of nitrobenzene.

In the present paper, an attempt has been made to investigate the influence of the introduction of one more nitro group in the ortho-, meta-, or para-position upon the spectrum of nitrobenzene.

Experimental

Materials.—*o*-Dinitrobenzene, Tokyo Kasei Co. guaranteed reagent, was used directly; m.p. 118.1°C (lit. 118°C). Commercial pure *m*-dinitrobenzene was recrystallized three times from ethanol; m.p. 90.4°C (lit. 90°C). *p*-Dinitrobenzene, Tokyo Kasei Co. guaranteed reagent, was recrystallized once from methanol; m.p. 174.7°C (lit. 174°C). Commercial guaranteed ethanol was fractionally distilled after the usual treatment.

Spectra.—The spectra of the dinitrobenzenes in ethanol were measured with a Hitachi quartz spectrophotometer, Model EPU-2 at room temperature. Path length of absorption cells was 1 cm.

Results and Discussion

As indicated in Fig. 1 and Table I, the maximum absorption band of *m*-dinitrobenzene is at a shorter wavelength and has a greater molar extinction coefficient than that of nitrobenzene, while the

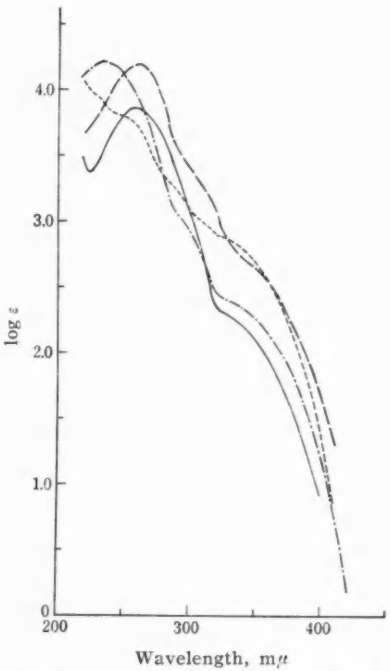

Fig. 1. Absorption spectra of nitrobenzene (——), *o*-dinitrobenzene (------), *m*-dinitrobenzene (—·—), and *p*-dinitrobenzene (— —), all in ethanol.

TABLE I. VALUES OF THE ABSORPTION MAXIMA OF DINITROBENZENES IN ETHANOL

	λ_{max}, mμ	ε
Nitrobenzene	260	8140
o-Dinitrobenzene	—	—
m-Dinitrobenzene	233	17200
p-Dinitrobenzene	261	15600

1) T. Abe, This Bulletin, **31**, 904 (1958).
2) T. Abe, ibid., **32**, 339 (1959).

absorption maximum of *p*-dinitrobenzene gives a more intense absorption band at the same region as the 260 mμ band of nitrobenzene. The 260 mμ band of nitrobenzene has been interpreted by Doub and Vandenbelt[3] and later by Wenzel[4] to correspond to the 200 mμ band of benzene which has the same intensity, but has been interpreted by Nagakura and Tanaka[5] in terms of the intramolecular charge transfer involving an excitation of a bonding electron of the highest occupied energy-level of benzene to the vacant energy-level of the nitro group.

From the concept of the intramolecular charge transfer, the maximum absorption bands of *m*- and *p*-dinitrobenzene will be discussed by considering interactions between the highest occupied energy-levels of nitrobenzene and the vacant level of the nitro group on substituting the second nitro group in the meta- or para-carbon atom of nitrobenzene. According to the energy level diagrams given by Nagakura and Tanaka[6,7], the vacant energy-level ($V_{NO_2} = -6.85$ eV.) of the nitro group is lower than the lowest vacant energy-level ($V_N = -4.65$ eV.) of nitrobenzene, to which the V_{NO_2} mainly contributes. On introducing one more nitro group in nitrobenzene, the energy-levels of nitrobenzene, indicated in Fig. 2, may be approximately affected by only the vacant level (V_{NO_2}) of the nitro group with such interaction as was given by Nagakura and Tanaka[5], because interactions with other occupied levels of the nitro group, which are remote or of different symmetry, are negligibly small. According to Nagakura and Tanaka's theory, as a result of the interaction with the V_{NO_2}, an energy-level ($E = H_{N1}$ or H_{N2}) of nitrobenzene shifts below by the following magnitude:

$$\Delta E = 1/2[(E - V_{NO_2}) + \{(E - V_{NO_2})^2 + 4C_N^2 C_{NO_2}^2 \beta^2\}^{1/2}] \quad (1)$$

Here C_N and C_{NO_2} are a coefficient of an atomic orbital of a carbon atom in the molecular orbital of E and a coefficient of an atomic orbital of the nitrogen atom in the molecular orbital of V_{NO_2}, respectively, where the carbon atom and the nitrogen one are joined together. The β is the resonance integral between the atomic orbital of the carbon atom and the orbital of the nitrogen atom. It is obvious that the ΔE increases as C_N increases or as $(E - V_{NO_2})$ decreases. On the other hand, the V_{NO_2} of the nitro group similarly interacts with the levels of nitrobenzene, especially with the H_{N1}, H_{N2} and the V_N that is nearest to the V_{NO_2}. When the nitro group is substituted in the meta-position of nitrobenzene, two intense absorption bands of intramolecular charge transfer can be expected to appear at longer wavelengths for *m*-dinitrobenzene owing to transitions involving excitations of bonding electrons of the occupied levels (H_{m1} and H_{m2}) to the lowest vacant level (V_m), because the V_{NO_2} interacts with both the levels of H_{N1} and H_{N2}, as in the case of some disubstituted benzenes[6]. On substituting the nitro group in the para-position of nitrobenzene, a transition of a bonding electron in H_{p2} to the lowest vacant level (V_p) can be predicted to show only an intense band of intramolecular charge transfer at a longer wavelength, the B_1-level (H_{N1}) in nitrobenzene being intact. The blue shift of 260 mμ band of nitrobenzene for

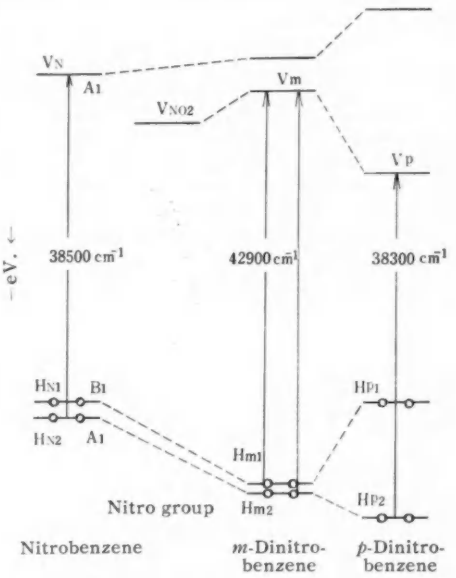

Fig. 2. Spectra of intramolecular charge transfer in dinitrobenzenes.

3) L. Doub and J. M. Vandenbelt, *J. Am. Chem. Soc.*, **69**, 2714 (1947).
4) A. Wenzel, *J. Chem. Phys.*, **22**, 1623 (1954).
5) S. Nagakura and J. Tanaka, ibid., **22**, 236 (1954); *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **75**, 331 (1954).
6) J. Tanaka and S. Nagakura, *J. Chem. Phys.*, **24**, 1274 (1956); *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **78**, 1200 (1957).
7) S. Nagakura and J. Tanaka, This Bulletin, **32**, 734 (1959).

m-dinitrobenzene means the great interaction of V_{NO_2} with H_{m1} and H_{m2}. Consequently, these levels will shift in nitrobenzene as indicated Fig. 2. In this case, the occupied B_1-level (H_{N1}) as well as the A_1-level (H_{N2}) in nitrobenzene may be predicted to become low in *m*-dinitrobenzene, because the coefficient of the atomic orbital belonging to the meta-carbon atom in the molecular orbital of the occupied B_1-level (H_{N1}) of nitrobenzene is greater than the corresponding coefficient in the A_1-level, although the H_{N1} is slightly higher than the H_{N2}. In the molecular orbital of the occupied A_1-level (H_{N2}) of nitrobenzene, the coefficient of the atomic orbital for the para-carbon atom is apparently greater than that for the meta-carbon atom. Accordingly, the A_1-level (H_{N2}) of nitrobenzene can be considered to become lower in *p*-dinitrobenzene than in *m*-dinitrobenzene, as given from Eq. 1. The maximum absorption band of *p*-dinitrobenzene lies at the wavelength close to that of nitrobenzene. From these it may be expected that the V_{NO_2}-level shifts below to the same extent, as compared with the H_{N2}, in *p*-dinitrobenzene, owing to the great interaction between the V_{NO_2} and the V_N. In comparison with the case of *m*-dinitrobenzene, it is known that the coefficient of the atomic orbital of the para-carbon atom is probably much greater than that of the meta-carbon atom in the molecular orbital of the vacant A_1-level (V_N) of nitrobenzene. From the above discussion, the maximum absorption bands of dinitrobenzenes may be interpreted to be owing to the electronic transitions illustrated in Fig. 2.

An ortho-substituted benzene usually shows a spectrum resembling that of a meta-substituted benzene[6], while the absorption curve of *o*-dinitrobenzene is different from that of *m*-dinitrobenzene, giving only shoulders at 250, 290, 310 and 360 mμ. This may be understood in terms of steric hindrance by the adjacent large nitro groups of *o*-dinitrobenzene. This steric hindrance may interfere with a coplanar arrangement of the nitro groups with benzene nucleus.

The weak shoulder of nitrobenzene at 290 mμ, which has been interpreted by Nagakura and Tanaka[6,8] to be related to the 260 mμ band of benzene, becomes more distinct in *m*- and *p*-dinitrobenzene.

The molar extinction coefficients of the 360 mμ bands for *o*- and *p*-dinitrobenzene are greater than those of *m*-dinitrobenzene, which are slightly larger than the corresponding molar extinction coefficient for nitrobenzene. The 360 mμ band of nitrobenzene has been interpreted by Wenzel[1] to be due to the nitro group.

Summary

In ethanol, *m*-dinitrobenzene shows the maximum absorption band at shorter wavelengths than nitrobenzene, while *p*-dinitrobenzene gives the absorption maximum at the wavelength near to that of nitrobenzene. These bands have briefly been discussed from the concept of the intramolecular charge transfer. The absorption curve of *o*-dinitrobenzene, indicating no absorption maximum but shoulders, are different from those of the other dinitrobenzenes, probably owing to steric hindrance by the adjacent large nitro groups.

The author is particulary indebted to Professor Yōkan Nomura for his suggestion and encouragement.

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8) J. Tanaka, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **79**, 1114 (1958).

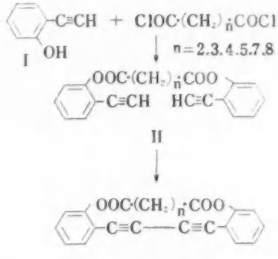
*Cyclic Acetylenes. I. Cyclic Derivatives of o,o'-Dihydroxydiphenyldiacetylene. An Example of a Strained Cyclic Diacetylene**

By Fumio TODA and Masazumi NAKAGAWA

(Received July 21, 1959)

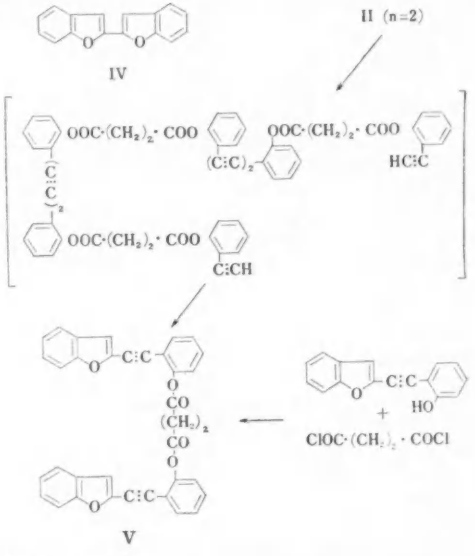
It is of interest to compare the physical and chemical properties of a strained acetylenic compound with that of a strainless analogue in relation to the reactive nature of benzyne intermediate[1]. Along with this line the authors have studied the synthesis of a cyclic diacetylene in which the structure of the molecule forces to bend the diacetylenic linkage. Recently a fairly large variety of cyclic polyacetylenes have been synthesized by several investigators[2], but most of these macrocycles seem to be strainless with regard to the triple bond.

A series of cyclic derivatives of *o,o'*-dihydroxydiphenyldiacetylene have been synthesized according to the following scheme. *o*-Hydroxyphenylacetylene (I)[3] was converted into the polymethylene dicarboxylate (II) by the reaction with the corresponding diacid dichloride in alkaline media. By oxidative coupling of II ($n=2$, 3, 4, 5, 7 and 8) according to the procedure of Eglinton[2] the authors have obtained III_a, III_b, III_c, III_d and $III_{d'}$ in 20, 40, 21 and 7.5% ($III_d+III_{d'}$) yield, respectively. Two isomers were found in the case of $n=7$. The low-melting isomer (III_d, m. p. 111°C) completely changed to the high-melting isomer ($III_{d'}$, m. p. 125~127°C) on standing at room temperature for two weeks.



The structures of compounds III were inferred from analyses, molecular weight determinations, ultraviolet and infrared spectroscopy. The cyclic nature of III was also confirmed by the absence of free ethynyl absorption in infrared spectra (ca. 3300 cm^{-1}) and by titration against silver nitrate.

In the case of $n=3$, 2,2'-dibenzofuranyl (IV)[4] was isolated in 25% yield together with III_a. IV was also obtained from the products of the coupling reaction of II ($n=2$) in 57% yield together with a small amount of compound V. The ultraviolet spectrum of V closely resembles that of 2-(2'-benzoyloxyphenylethynyl)-benzofurane[4] as illustrated in Fig. 1. The structure of V was confirmed by the



* For a preliminary announcement of a part of this work, see *Chem. & Ind.*, **1959**, 458.

1) G. Wittig, *Angew. Chem.*, **68**, 245 (1957); J. D. Roberts, "Chemical Society Symposia Bristol 1958", The Chemical Society, London (1958), p. 115.

2) G. Eglinton and A. R. Galbraith, *Chem. & Ind.*, **1956**, 737; *J. Chem. Soc.*, **1959**, 889; F. Sondheimer, Y. Amiel and R. Wolovsky, *J. Am. Chem. Soc.*, **79**, 4274 (1957) and preceding papers.

3) V. Prey and G. Pieh, *Monatsh. Chem.*, **80**, 790 (1949).

4) F. Toda and M. Nakagawa, This Bulletin, **32**, 514 (1959).

identity with a synthetic specimen which was obtained by the reaction of 2-(2'-hydroxyphenylethynyl)-benzofurane[4] and succinic acid dichloride in alkaline media.

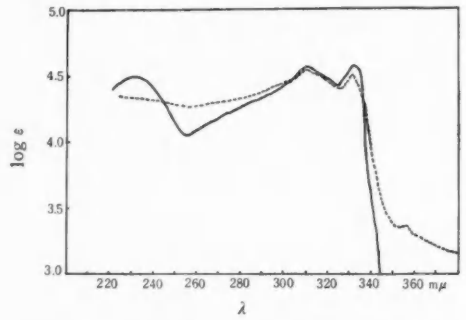
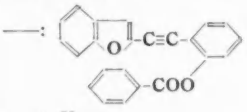


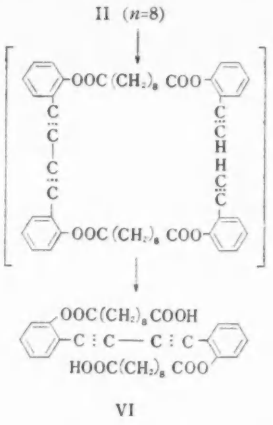
Fig. 1. The ultraviolet spectra of 2-(2'-benzoyloxyphenylethynyl)-benzofurane and V. The curve of V was drawn using the reduced ε values corresponding to the diyne-unit.



----: V

The mechanism of the formation of IV is not yet clear, but it may be formed from highly strained III cleaving the ester linkages simultaneously accompanying the benzofurane ring formation. It has been reported by the present authors that IV is formed in a quantitative yield from *o*, *o'*-dihydroxydiphenyldiacetylene on treatment with alkali[4]. IV and adipic acid are formed on the alkaline hydrolysis of III_b, but the formation of IV from *o*, *o'*-dihydroxydiphenyldiacetylene under the condition of Eglinton's oxidative coupling was not observed. Therefore, the simple interpretation such as the intramolecular cyclization to IV of *o*, *o'*-dihydroxydiphenyldiacetylene which is formed by the ring fission of the cyclic diyne is not acceptable as the mechanism of the formation of IV under the condition of the coupling reaction. Also the formation of V may be attributed to the fission of the ester linkages presumably in the course of cyclic trimerization of II (n=2).

The attempt to prepare III (n=8) have failed. In this case the only identified product was VI, and the formation of VI is also probably associated with the fission of the ester linkages during the course of cyclic dimerization of II (n=8).



VI

The most striking property of III_a is its high sensitivity to light in the solid state making a sharp contrast to the photostable nature of III_b, III_c, III_d and $III_{d'}$. The surface of the colorless crystals of III_a was rapidly coated with red colored, insoluble and high melting point material when the solid was exposed to a diffused light in the laboratory. But the solution of III_a was found to be fairly stable. These properties are closely related to those of some polyacetylene compounds[5].

Examination of the scale models of III indicates that III_b is a rigid and planar molecule with the two phenyl groups held in the same plane. On the other hand, the phenyl groups in III_c are not readily able to become coplanar on account of the bridging chain. The model of III_a clearly shows that the diacetylenic linkage is forced to bend owing to the short methylene chain holding its phenyl groups in a coplanar position. The anomalous photosensitivity of III_a may be attributed therefore to the bending of the diacetylenic bond. It has already been suggested by Bohlmann that the stabilization of a certain polyacetylenic compound bearing two bulky terminal groups is associated with the steric effect of the bulky groups retarding the formation of cross linkings[6]. The diacetylenic linkage in III_a seems to be more exposed to the outer environment of the molecule on account of its bending as compared with that linkage of the corresponding less strained cyclic diynes. Therefore the intermolecular approach to form cross linkings which is facilitated

5) Cf. J. B. Armitage, C. L. Cook, N. Entwistle, E. R. H. Jones and M. C. Whiting, *J. Chem. Soc.*, 1952, 1998.
6) F. Bohlmann and E. Inhoffen, *Chem. Ber.*, **89**, 1276 (1956).

by the presence of the distorted diacetylenic bond is, though it is not decisive, a possible cause of the unstable nature of III_a.

The catalytic reduction of 2,2'-diacetoxydiphenyldiacetylene (VII), III_a and III_b were carried out using a palladium on charcoal catalyst. It was hoped that III_a might exhibit some abnormalities in the course of hydrogenation resulting from the ring strain, but the experimental results indicated no marked difference in the rates of hydrogenation as illustrated in Fig. 2. The fact that the hydrogenation of III_a stopped after absorption of ca. 90% of theoretical amount of hydrogen is probably ascribed to the formation of minor amount of the above mentioned photopolymer during the course of reduction.

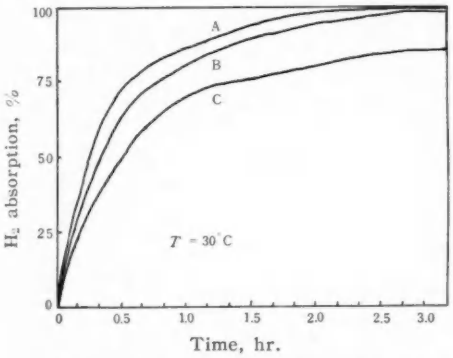


Fig. 2. The rates of hydrogenation of VII, III_a and III_b.
A: VII B: III_b C: III_a

These situations seem to be reflected in the ultraviolet spectra of III_a, III_b, III_c and III_d. VII was used as a comparison for an open chain analogue of III. As indicated in Table I and Fig. 3, the ultraviolet spectra of these diacetylene are closely related and are different only in the absorption intensities without any significant wavelength displacements. The extinction coefficients ε of λ_{max} of the long wavelength region (290~340 mμ) of III_b are larger than that of VII, but the ε values of III_a, III_c, III_d and $III_{d'}$ in the same region are smaller than that of VII.

TABLE I

Compound	Absorption							
VII			250 (479)	260 (483)	275 (240)	291 (337)	310 (445)	331 (398)
III_a	229.5 (304)	**235** (260)			**275** (88)	292 (198)	310 (322)	331 (292)
III_b					275 (113)	291 (290)	310 (535)	332 (541)
III_c			248.5 (267)		**275** (122)	293 (171)	310 (216)	331 (174)
III_d			248 (301)	260 (304)	275 (152)	290 (227)	309 (337)	331 (304)
$III_{d'}$			249 (325)	260 (322)		292 (197)	310 (241)	331 (200)
V							310 (343)*	331 (315)*
VI			250 (361)	260 (364)	**275** (155)	292 (204)	310 (248)	331 (216)
$VIII_a$			250 (305)	260 (316)	275 (153)	290 (219)	309 (288)	331 (255)
$VIII_b$			250 (277)	260 (284)	275 (124)	291.5 (205)	309.5 (284)	331 (244)
IX_a				260 (294)	275 (112)	**310** (207)	326 (316)	349 (267)
IX_b				260 (272)	275 (95)	**310** (190)	327 (293)	349 (251)
X_a			**240** (204)	260 (213)	**275** (85)	305 (168)	323 (270)	345 (236)
X_b			**240** (204)	260 (216)	**275** (97)	**305** (166)	323 (252)	345 (218)

The figures indicate the λ_{max} in mμ.
The figures in parentheses are $\varepsilon_{max} \times 10^{-2}$.
Asterisk indicates the ε value of per dyne unit.
The bold figures indicate shoulders.
All spectra were measured in 95% ethanol.

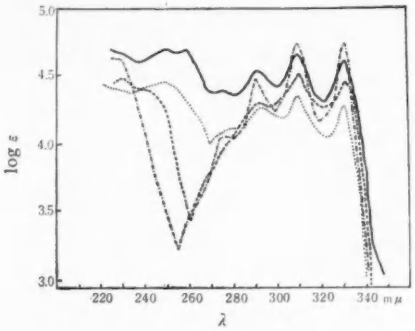
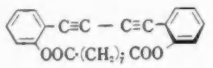


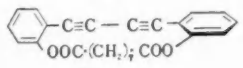
Fig. 3. The ultraviolet spectra of VII and the cyclic diacetylenes (III_a, III_b and III_c).
——: VII ----: III_a
-·-·: III_b ·····: III_c

The decrease of the ε values are in the sequence of $III_b > VII > III_a > III_c$ indicating the important role of the uniplanar phenyl groups in affecting the intensity of absorption. This fact suggests that the spectra associate with transitions between non-planar ground states and near planar excited states[7]. The largest ε values of III_b in this region may be due to the rigid and planar structure of the molecule having maximum conjugation between the two phenyl groups and the acetylenic bonds. On the other hand, the smaller ε values of III_a as compared with VII may be attributed to the diminished probability of excitation of the molecule to an excitation state in which the diacetylenic linkage should take a linear configuration. The low intensity of absorption of III_c, III_d and $III_{d'}$ may also be regarded as the twisted position of the phenyl groups in these molecules affecting to reduce the probability to a uniplanar state of excitation.

The ultraviolet spectra of III_d and $III_{d'}$ are different as shown in Table I and Fig. 4. The absorption intensity in the long wavelength region of $III_{d'}$ is much lower than that of III_d indicating the presence of a larger degree of twist of the phenyl groups in $III_{d'}$ as illustrated in the following formulae. Examination of the scale models of III_d and $III_{d'}$ indicates that the methylene chain in III_d is much more crowded than in $III_{d'}$. Therefore, the relief of compression energy of methylene chain seems to be responsible to the



III_d



$III_{d'}$

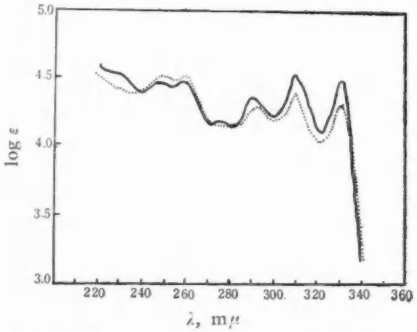
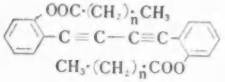


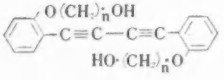
Fig. 4. The ultraviolet spectra of the isomeric cyclic diacetylene (III_d and $III_{d'}$).
——: III_d ·····: $III_{d'}$

stabilization of III_d to $III_{d'}$. The isolation of III_d and $III_{d'}$ may be regarded as the first example of the presence of a new type of conformational isomers in which the diacetylenic linkage behaves as pivot bond.

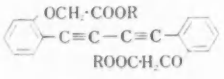
The low absorption intensity in the ultraviolet spectrum of VI is also explained by the hypochromic effect of non-coplanar



VII : n=0
$VIII_a$: n=1
$VIII_b$: n=2



IX_a : n=2
IX_b : n=3



X_a : R=CH_3
X_b : R=C_2H_5

7) E. Braude, F. Sondheimer and W. F. Forbes, *Nature*, **173**, 117 (1954); Also cf. E. Heilbronner and R. Gerdil, *Helv. Chim. Acta*, **39**, 1996 (1956).

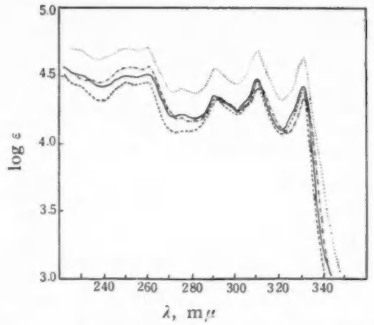


Fig. 5. The ultraviolet spectra of 2,2'-diacyloxydiphenyldiacetylenes.
·····: VII ——: $VIII_a$
– – –: $VIII_b$ –·–·: VI

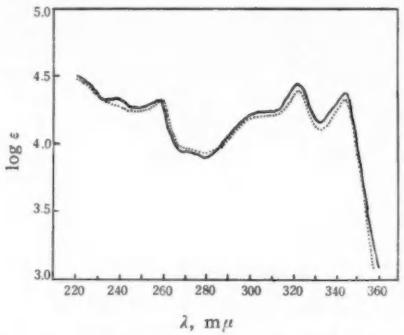


Fig. 7. The ultraviolet spectra of 2,2'-di-(alkyloxycarbonylmethoxy-diphenyldiacetylenes.
——: X_a ·····: X_b

phenyl groups. Further examples of the effect are obtained in the series of VIII, IX and X. As illustrated in Fig. 5 and Table I, the increase in the number of methylene group in VIII resulted in the decrease of the intensity of absorption. The steric effect of the acyl group affecting the hypochromic shift of the ultraviolet spectra of VIII seems to show a tendency approaching to a definite value when the steric requirement of the group reaches a certain degree, namely, the differences of ε values between VII and $VIII_a$, $VIII_b$ and the differences between VII and VI are quite large, while the difference between $VIII_a$ and $VIII_b$ and that of VI and $VIII_a$, $VIII_b$ are relatively small.

The same trend is also observed in the case of IX_a, IX_b, X_a and X_b as indicated in Figs. 6 and 7 and in Table I.

The characteristic feature in the ultraviolet spectra of III_a and III_b are the presence of a sharp and intense λ_{min} at ca. 260 mμ, the ε values are only one-tenth of the corresponding ε of III_c and III_d. The proximity effect of *o,o'*-bridging chain which is held closely parallel with the diacetylenic linkage may be a possible explanation of this fact, but it is premature to deduce a conclusion from these few examples.

Further studies in the same direction are now in progress.

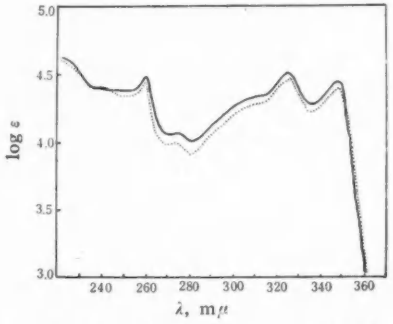


Fig. 6. The ultraviolet spectra of 2,2'-di-ω-hydroxyalkyloxydiphenyldiacetylenes.
——: IX_a ·····: IX_b

Experimental**

General Procedure of the Preparation of Di-*o*-ethynyl-phenyl Polymethylene Dioate (II, *n*=2, 3, 4, 5, 7 and 8).—Polymethylene dioic acid chloride (2 mol.) was added to the solution of *o*-hydroxyphenylacetylene[4] (I, 1 mol.) in 10% aqueous solution of potassium hydroxide (7 equiv.). The mixture was shaken under ice cooling. The oily material separated was extracted with ether, washed with aqueous potassium hydroxide and water successively. The colorless viscous oil obtained on evaporating the solvent was used without further purification. For example, in the case of *n*=7, azelaic acid chloride (9.0 g., 0.04 mol.) was added in one portion to the solution of I (2.4 g., 0.02 mol.) in 10% aqueous solution of potassium hydroxide (7.8 g., 0.14 mol.), and the mixture was shaken for 1 hr. The reaction mixture was extracted with ether, washed with aqueous potassium hydroxide and water. The ether extract was dried over anhydrous magnesium sulfate. A colorless oil was obtained by the evaporation of the solvent (3.3 g., 85%). The crude II [*n*=7, I.R. max., 3260 (-C≡CH), 2860, 2920 (-CH_2-), 1762 cm^{-1} (ester)] gave yellow cuprous acetylide by Ilosvay's reagent, and gave white silver salt by an alcoholic silver nitrate solution.

Oxidative Coupling of Di-*o*-ethynylphenyl Adipate (*n*=4). — The mixture of II (*n*=4, 1.5 g.), cupric

** Not all melting points are corrected. Infrared spectra were measured using liquid film or nujol mull method.

acetate monohydrate (15 g.) and pyridine (150 g.) was stirred for 4 hr. at 55°C. The stirring was continued for additional 1 hr. at room temperature. Most of the pyridine was removed from the reaction mixture under reduced pressure. Water (1000 ml.) was added to the residue and extracted with ether (1000 ml.). The ether extract was washed with aqueous cupric acetate and water, successively. The ethereal solution was dried over anhydrous magnesium sulfate. The solvent was removed and the residual solid was recrystallized from ethanol giving III_b (0.6 g., 40%) as colorless needles, m. p. 123.5°C.

Anal. Found: C, 76.83; H, 4.54; mol. wt. (Rast), 325. Calcd. for $C_{22}H_{16}O_4$: C, 76.73; H, 4.68%; mol. wt., 344.

I. R. max., 1758 cm^{-1} (ester).

III_b gave no precipitation with alcohlic silver nitrate solution.

Hydrolysis of III_b. — III_b (0.1 g.) was dissolved in an aqueous alcoholic solution of potassium hydroxide (ethanol 15 ml., water 2 ml. and potassium hydroxide 0.3 g.). The solution was refluxed for 3 hr. on a boiling water bath. The crystals were recrystallized from ethanol yielding colorless needles, m. p. 194.5~195.5°C which showed no depression of the mixed melting point with an authentic sample of 2,2'-dibenzofuranyl (IV)[4]. The filtrate was washed with ether and the aqueous layer was acidified with 2 N hydrochloric acid, extracted with ether. Treatment of the ether extract gave adipic acid, m. p. 148~150°C. The mixed melting point with pure adipic acid showed no depression.

Oxidative Coupling of Di-*o*-ethynylphenyl Glutarate (II, $n=3$). — II ($n=3$, 2.5 g.) was mixed with cupric acetate monohydrate (20 g.) and pyridine (200 g.). The mixture was agitated for 4 hr. at 55°C. The insoluble precipitate was removed from the reaction mixture by filtration and was washed with ether. The filtrate was distilled under reduced pressure to remove pyridine. The residue was extracted with ether (600 ml.). The ether extract and the ethereal washing was combined and washed with a saturated aqueous solution of cupric acetate and water. The ether solution was dried over anhydrous magnesium sulfate and concentrated to 100 ml. The crystals deposited at this stage were filtered (m. p. 194.5~195.5°C, 0.2 g.). The crystals were identified as 2,2'-dibenzofuranyl (IV) by the mixed melting point determination. The solvent was removed from the filtrate and the residue was recrystallized from ethanol employing active charcoal, giving colorless needles mixed with hexagonal plates. Further recrystallization of the mixed crystals from ethanol (50 ml.) gave 0.2 g. of IV. The total yield of IV was found as 0.4 g. (25%). Slightly impure III_a was obtained as hexagonal plates (m. p. 133~134°C, 0.5 g., 20%) on standing the alcoholic filtrate. Recrystallization of this material gave pure III_a, m. p. 135~136°C.

Anal. Found: C, 76.33; H, 4.08; mol. wt. (Rast), 350. Calcd. for $C_{21}H_{14}O_4$: C, 76.35; H, 4.27%; mol. wt., 330.

I. R. max., 1755 cm^{-1}.

The surface of the crystals of III_a changed to red on exposure to a diffused light in the laboratory. An amorphous, high melting material remained when the colored crystals were dissolved in ethanol.

Oxidative Coupling of Di-*o*-ethynylphenyl Pimelate (II, $n=5$). — II ($n=5$, 1.4 g.) was oxidized with cupric acetate monohydrate (1.5 g.) in pyridine (150 g.) at 55°C. After 3 hr., the reaction mixture was treated similarly as described above yielding a viscous oil (1.3 g.). The mixture of the oil with methanol (2 ml.) gradually solidified on standing. Repeated recrystallization from methanol using active charcoal gave III_c as colorless needles, m. p. 120.5~121.5°C, 0.3 g (21%).

Anal. Found: C, 76.94; H, 5.06; mol. wt. (Rast), 364. Calcd. for $C_{23}H_{18}O_4$: C, 77.08; H, 5.06%; mol. wt., 358.

I. R. max., 1760 cm^{-1}.

III_c gave no precipitation with alcoholic silver nitrate.

***o*, *o'*-Diacetoxydiphenyldiacetylene (VII).** — Acetic anhydride (2.0 g.) was introduced in one portion to the solution of *o*, *o'*-dihydroxydiphenyldiacetylene (0.4 g.) in aqueous potassium hydroxide (water 40 ml., potassium hydroxide 1.4 g.). The mixture was shaken under ice cooling. The solid deposited was collected by filtration and recrystallized from ethanol yielding VII as colorless needles, m. p. 134°C.

Anal. Found: C, 75.33; H, 4.31. Calcd. for $C_{20}H_{14}O_4$: C, 75.46; H, 4.43%.

I. R. max., 1755 cm^{-1} (ester).

Oxidative Coupling of Di-*o*-ethynylphenyl Succinate (II, $n=2$). — The mixture of II ($n=2$, 2.5 g.) was stirred for 3 hr. at 55°C and the stirring was continued further 30 min. at room temperature. The most of pyridine was removed under reduced pressure. Water was added to the residue and the mixture was extracted with ether (1000 ml.). The extract was washed with saturated solution of cupric acetate and water, successively. The dried ether extract was reduced to 100 ml. and the needle-like crystals deposited (0.4 g., m. p. 194.5~195.5°C) were collected by filtration. This was identified as IV by mixed melting point determination. The solvent was removed from the filtrate resulting in a mixture of viscous oil and crystals. The crystals separated by filtration were washed with hot ethanol, giving IV (0.7 g.). The recrystallization of the combined IV from benzene using charcoal, yielded 1.0 g. (57%) of IV. The oily filtrate gradually solidified on standing. The solid was treated with ethanol and charcoal to result in V, colorless needles, m. p. 157.5~158.5°C, 20 mg. (ca. 1%).

Anal. Found: C, 78.23; H, 4.09; mol. wt. (Rast), 517. Calcd. for $C_{36}H_{22}O_6$: C, 78.54; H, 4.03%; mol. wt., 550.

I. R. max., 1755 cm^{-1} (ester).

V gave a negative test against alcoholic silver nitrate.

Synthesis of Di-2-(2'-benzofuranylethynyl)-phenyl Succinate (V). — 2-(2'-Hydroxyphenylethynyl)-benzofurane[4] (50 mg.) was dissolved in the solution of potassium hydroxide (0.35 g.) in water (10 ml.). Succinoyl chloride (0.31 g.) was added in one portion to the alkaline solution and was shaken to result in a crystalline solid. The solid was collected by filtration, washed with water and alcohol. Recrystallization from ethanol gave colorless needles, m. p. 157.5~158.5°C, 30 mg. (51%). The mixed melting point with V, the product of the oxidative coupling of II (n=2), showed no depression. The infrared spectra of these two substances were found as identical over the entire region of wavelength.

Oxidative Coupling of Di-*o*-ethynylphenyl Nonanedioate (II, n=7). — The mixture of II (n=7, 2.0 g.), cupric acetate monohydrate (15 g.) and pyridine (150 g.) was stirred for 3.5 hr. at 55°C. Pyridine was removed under reduced pressure. Water (1000 ml.) was added to the residue and the mixture was extracted with ether (1000 ml.). The ethereal layer was washed with saturated solution of cupric acetate and water, successively, and dried over anhydrous magnesium sulfate. A viscous oil (0.5 g.) obtained by removing the solvent was mixed with ethanol (2.0 ml.). The mixture was kept to result crystallization. The crystals were collected by filtration (filtrate A). The crystals were recrystallized from ethanol and separated by filtration (filtrate B). Further recrystallization from ethanol gave III_d as colorless needles, m. p. 125~127°C, 50 mg. (2.5%).

Anal. Found: C, 77.20; H, 5.73. Calcd. for $C_{25}H_{22}O_4$: C, 77.70; H, 5.74%.

The crude crystals obtained by the concentration of the combined filtrates A and B were treated with ethanol and charcoal and recrystallized from ethanol, resulting in III_d as colorless needles, m. p. 111°C, 100 mg. (5%).

Anal. Found: C, 77.56; H, 5.68; mol. wt. (Rast), 399. Calcd. for $C_{25}H_{22}O_4$: C, 77.70; H, 5.74% mol. wt., 386.

After being kept for two weeks at room temperature the melting point of III_d raised to 125~127°C and the mixed melting point of the material with $III_{d'}$ showed no depression. The ultraviolet spectra of III_d and $III_{d'}$ measured after 4 days from the isolation are listed in Table I.

Oxidative Coupling of Di-*o*-ethynylphenyl Decanedioate (II, n=8). — II (n=8, 2.5 g.) was treated with cupric acetate monohydrate (15 g.) in pyridine (200 g.) at 55°C for 4 hr. The same treatment of the reaction mixture as stated in the case of II (n=7) resulted a crystalline solid. Recrystallization of the solid from ethanol employing charcoal yielded VI as amorphous powder, m. p. 149~151.5°C, 0.3 g. (16%).

Anal. Found: C, 72.29; H, 6.83. Calcd. for $C_{36}H_{42}O_8$: C, 71.74; H, 7.02%.

I. R. max. (measured in hexachlorobutadiene), 2920, 2850 (-CH_2-), 2650 (carboxyl OH), 1755 (ester) and 1703 cm^{-1} (carboxyl CO).

VI is readily soluble in aqueous sodium hydrogen carbonate and sodium hydroxide solution and gave a negative test against an ethanolic silver nitrate.

2,2'-Dipropionyloxydiphenyldiacetylene ($VIII_a$). — Propionic anhydride (2.6 g.) was added in one portion to the solution of 2,2'-dihydroxydiphenyldiacetylene[4] (0.47 g.) in water (20 ml.) and potassium hydroxide (1.6 g.). The mixture was shaken with occasional cooling with ice water. The solid separated was recrystallized from ethanol to result in $VIII_a$, m. p. 56°C, 0.5 g. (70%).

Anal. Found: C, 76.06; H, 5.29. Calcd. for $C_{22}H_{18}O_4$: C, 76.28; H, 5.24%.

I. R. max., 1770 cm^{-1} (ester).

2,2'-Dibutylyloxydiphenyldiacetylene ($VIII_b$). — 2,2'-Dihydroxydiphenyldiacetylene (1.2 g.) was reacted with butyric anhydride (8.0 g.) according to the same procedure described above for the preparation of $VIII_a$. The reaction mixture was extracted with ether and the extract was washed with aqueous alkali and water. The solvent was evaporated from the dried extract yielding crude crystals. Recrystallization of the crude material from aqueous ethanol resulted in $VIII_b$, m. p. 51°C, 1.4 g. (75%).

Anal. Found: C, 76.61; H, 5.93. Calcd. for $C_{24}H_{22}O_4$: C, 76.98; H, 5.92%.

I. R. max., 1755 cm^{-1} (ester).

2,2'-Di-(β-hydroxyethoxy)-diphenyldiacetylene (IX_a). — The reaction of *o,o'*-dihydroxydiphenyldiacetylene with ethylenechlorohydrine in the presence of sodium ethoxide gave IX_a. IX_a thus obtained was separated into two forms, labile form (m. p. 75~76°C) and stable form (m. p. 90~91°C). The labile crystals readily changed to the stable form on standing at room temperature.

Anal. Found: C, 74.64; H, 5.57. Calcd. for $C_{20}H_{18}O_4$: C, 74.52; H, 5.63%.

I. R. max., 3350 (-OH), 2145 (-C≡C-) and 1244 cm^{-1} (=C-O-).

2,2'-Di-(γ-hydroxypropoxy)-diphenyldiacetylene (IX_b). — *o*-(γ-Hydroxypropoxy)-phenylacetylene (b. p. 142~143°C/7 mmHg) which was obtained in 88% yield by the reaction of *o*-hydroxyphenylacetylene[1] and 3-bromo-1-propanol in the presence of sodium ethoxide was oxidatively coupled according to the method of Sörensen[8]. Treatment of the reaction mixture resulted in IX_b as colorless needles in 57% yield, m. p. 103°C.

Anal. Found: C, 75.54; H, 6.01. Calcd. for $C_{22}H_{22}O_4$: C, 75.41; H, 6.33%.

I. R. max., 3320 (-OH), 2145 (-C≡C-), 1252 cm^{-1} (=C-O-).

2,2'-Di-(alkyloxycarbonylmethoxy)-diphenyldiacetylene (X_a and X_b). — The reaction of *o,o'*-dihydroxydiphenyldiacetylene with methyl bromoacetate in the presence of sodium ethoxide resulted in X_a as colorless needles in 75% yield, m. p. 143°C.

Anal. Found: C, 70.04; H, 4.90. Calcd. for $C_{22}H_{18}O_6$: C, 69.83; H, 4.80%.

I. R. max., 1745 cm^{-1} (ester).

X_b was prepared in the same manner employing

8) T. Bruun, T. Morthei and N. A. Sörensen, *Acta Chem. Scand.*, **4**, 850 (1950).

ethyl bromoacetate, m. p. 98.5~99°C, colorless needles.

Anal. Found: C, 70.57; H, 5.36. Calcd. for $C_{24}H_{26}O_6$: C, 70.92; H, 5.46%.

The authors are grateful to the Shiono Perfume Industry Co., Osaka for generous quantities of coumalin and to Messrs. T. Shiba and M. Okumiya and Miss K. Koike for performing the elementary analyses.

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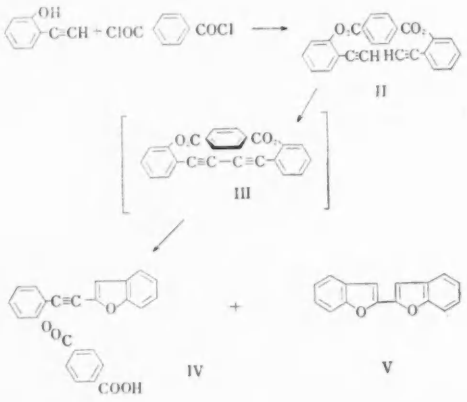
Cyclic Acetylenes. II. Attempted Synthesis of Cyclic Terephthalate of o,o'-Dihydroxydiphenyldiacetylene

By Fumio TODA and Masazumi NAKAGAWA

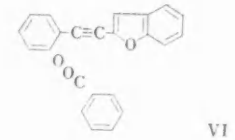
(Received July 21, 1959)

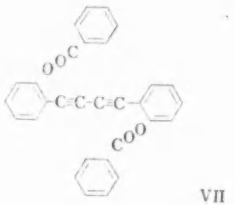
Cyclic terephthalate of *o,o'*-dihydroxydiphenyldiacetylene (III) may offer a suitable model substance for the investigation of transannular phenomena between the π-electron system of the benzene nucleus of terephthalic acid residue and that of diacetylenic linkage, because the scale model of this molecule indicates that the molecule is rigid, holding the terephthalate group closely in parallel with the diacetylenic linkage.

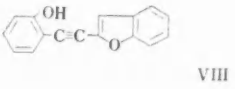
The synthesis of III has been attempted according to the following series of reactions. Di-2-ethynylphenyl terephthalate (II) was obtained in good yield by the reaction of *o*-hydroxyphenylacetylene (I)[1] with terephthaloyl chloride in aqueous acetone in the presence of sodium hydroxide.



The oxidative coupling according to the Eglinton's procedure[2] at a reaction temperature of 55°C resulted in 2-(2'-benzofuranylethynyl)-phenyl hydrogen terephthlate (IV) in 5% yield. 2, 2'-Dibenzofuranyl (V)[3] and IV were isolated from the reaction products in 15 and 3% yield, respectively, when the reaction was carried out at a temperature of 60°C.







1) V. Prey and G. Pieh, *Monatsh. Chem.*, **80**, 790 (1949).
2) G. Eglinton and A. R. Galbraith, *Chem. & Ind.*, **1956**, 737.
3) F. Toda and M. Nakagawa, This Bulletin, **32**, 514 (1959).

The ultraviolet spectra of VIII[3] have three maxima in the long wavelength region (290~340 mμ), whereas the spectra of VI and di-2-(2'-benzofuranylethynyl-phenyl succinate[4] have only two peaks in the same region lacking the maximum at ca. 290 mμ indicating that the presence of the free hydroxyl group is responsible for the appearance of the maximum at ca. 290 mμ in the ultraviolet spectra of 2-phenylethynylbenzofurane type compounds. On the other hand, ester derivatives of *o,o'*-dihydroxydiphenyldiacetylene such as VII and *o,o'*-diacetoxydiphenyldiacetylene have always three λ_{max} in the long wavelength region. The ultraviolet spectrum of IV is closely related to that of VI lacking the absortion near 290 mμ (cf. Table I; Figs. 1 and 2). The infrared spectrum of IV indicates the presence of a carboxyl group (ν_{OH}, 2655, 2520 cm^{-1}; ν_{CO}, 1696 cm^{-1}) and ester group (ν_{CO}, 1735 cm^{-1}). From these findings the structure of hydrogen terephthalate of VIII was assigned to IV. Presumably internal strains resulting from steric or a dipolar replusion between the terephthalate group and the diacetylenic bond caused the cleavage of one or both of the ester linkage of III yielding IV or V. The same type of fission of ester linkage during the course of intramolecular oxidative coupling of a series of dialkynyl terephthalate was recently reported by Eglinton and Galbraith[5].

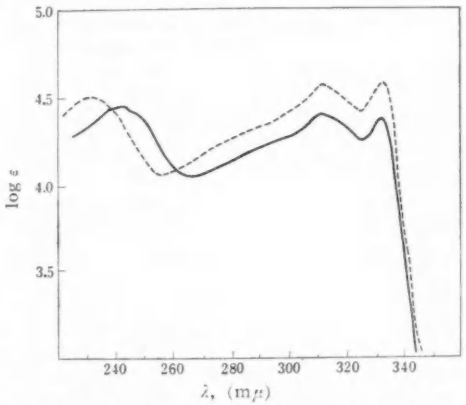


Fig. 1. The ultraviolet spectra of 2-[2'-(*p*-carboxybenzoyloxy)-phenylethynyl]-benzofurane (IV) and 2-(2'-benzoyloxyphenylethynyl)-benzofurane (VI).
——: IV ------: VI

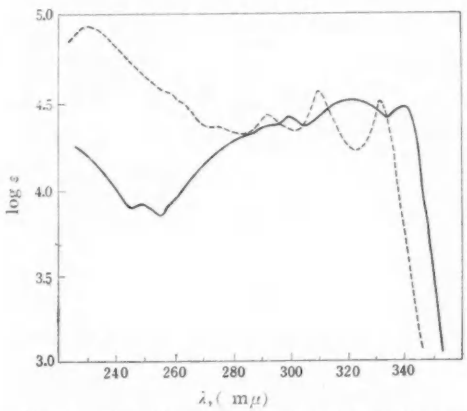


Fig. 2. The ultraviolet spectra of 2,2'-dibenzoyloxydiphenyldiacetylene (VII) and 2-(2'-hydroxyphenylethynyl)-benzofurane (VIII).
------: VII ——: VIII

TABLE I

Compound	Absorption, mμ				
IV	242 (282)			311 (253)	332 (245)
VI	230 (308)			311 (364)	332 (371)
VII	230 (815)	**275** (229)	293 (265)	311 (346)	332 (299)
II	240 (1075)	**270** (146)			
VIII	250 (79)		298 (265)	318 (297)	340 (284)

All spectra were measured in 95% ethanol. The figures in parentheses are $\varepsilon_{max} \times 10^{-2}$. The bold figures indicate shoulder.

It is interesting to note that the infrared spectrum of VIII shows the absorption of disubstituted acetylenic bond at 2207 cm^{-1}, but the corresponding absorption disappears in the spectra of IV, VI and VII. The low intensity of absorption in ultraviolet region of IV, as compared with that of VI, is attributable to the hypochromic influence of the more bulky terephthalic acid group as discussed in the previous paper of the series[4].

Further studies on the synthesis of cyclic derivatives of *o,o'*-dihydroxydiphenyldiacetylene containing a para-disubstituted benzene as the *o,o'*-bridging chain are now in progress.

Experimental*

2-Ethynylphenyl Terephthalate (II).—*o*-Hydroxyphenylacetylene (I, 0.6 g) was dissolved in a mixture of sodium hydroxide (0.2 g.), acetone (10 ml.)

4) F. Toda and M. Nakagawa, This Bulletin, **33**, 223 (1960).

5) G. Eglinton and A. R. Galbraith, *J. Chem. Soc.*, **1959**, 889.

* Not all melting points are corrected.

and water (1.0 ml.). Terephthaloyl chloride (0.5 g.) in acetone (10 ml.) was added to the solution at a time. The mixture was shaken with occasional cooling with ice. The solid deposited was filtered to yield somewhat crude II, m.p. 177°C (decomp.), 0.9 g. (97%), which was recrystallized from ethanol to give pure II, colorless leaflets, m.p. 177.5°C (decomp.).

Anal. Found: C, 78.25; H, 3.70. Calcd. for $C_{24}H_{14}O_4$: C, 78.68; H, 3.85%.

I.R. max., 3265 cm^{-1} ($-C\equiv CH$), 1741 cm^{-1} (ester), 1248, 1264 cm^{-1} ($=C-O-$).

II gives yellow cuprous acetylide with Ilosvay's reagent and white silver salt with ethanolic silver nitrate solution.

Oxidative Coupring of II at 55°C.—II (2.0 g.) in pyridine (50 g.) was added to the solution of cupric acetate monohydrate (15 g.) in pyridine (100 g.). The mixture was kept at 55°C for 5 hr. The precipitate was removed and most of the solvent was removed under reduced pressure. The residue was mixed with water (1000 ml.) and extracted with ether (1000 ml.). The extract was washed with a saturated solution of cupric acetate and water, successively. The dried ethereal solution was concentrated to 100 ml., and the greenish yellow precipitate formed was removed. Concentration of the filtrate yielded crude crystals. After treatment with acetone and charcoal, the crude material was repeatedly recrystallized from xylene to give pure IV, colorless needles, m.p. 222.5~223°C (decomp.), 0.1 g. (5%).

Anal. Found: C, 75.38; H, 3.86; mol. wt. (Rast), 343. Calcd. for $C_{24}H_{14}O_5$: C, 75.39; H, 3.69%; mol. wt., 382.

Oxidative Coupling of II at 60°C.—II (3.0 g.) in pyridine (150 g.) was added through a Hershberg type dropping funnel to the vigorously stirred solution of cupric acetate monohydrate (15 g.) in pyridine (150 g.) at 60°C over a period of 4 hr., and stirring was continued for additional 1.5 hr. at the same temperature. The precipitate formed was removed by filtration. After removal of pyridine in vacuo, the residue was diluted with water and extracted with benzene (400 ml.). The benzene layer was treated according to the usual manner. Evaporation of the solvent gave a greenish black solid. The solid was digested with ether, and the solvent was removed to give crystals, which were refluxed with ethanol (20 ml.) and the insoluble material was removed by filtration. The filtrate was cooled to yield crystals, which were repeatedly recrystallized from xylene to yield IV, m.p. 222.5~223°C (decomp.), 100 mg. (3%). On concentration of the mother liquor, V, colorless needles, m.p. 190~194°C, 0.3 g. (15%) was obtained, which undepressed the melting point of an authentic sample[3].

The authors wish to thank Messrs. T. Shiba and M. Okumiya and Miss K. Koike for performing the elementary analyses.

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High Pressure Reduction of Organic Compounds with Urushibara Catalyst. VI[1]. *A New Type of Urushibara Nickel Catalyst*

By Izumi MOTOYAMA

(Received August 15, 1959)

In 1952 Urushibara and Chuman discovered a new catalyst, which was prepared from precipitated nickel. Aqueous nickel chloride solution was treated with zinc dust, and the precipitated nickel was digested with caustic alkali to obtain the active catalyst for hydrogenation[2]. The procedure for the preparation of this catalyst has been successively modified to obtain the more active catalyst. It was also found that a highly active catalyst can be obtained by digesting the precipitated nickel with either aqueous caustic alkali or aqueous acetic acid, and the former was named Urushibara nickel B or U-Ni-B in abbreviation[3], and the latter Urushibara nickel A or U-Ni-A in abbreviation[4]. Recently it was proved that the activity of the U-Ni-B is comparable with that of Raney nickel catalyst for hydrogenation under ordinary pressure[5].

An application of Urushibara nickel catalyst to the hydrogenation of various organic compunds under high pressure

1) Part V: K. Hata, S. Taira and I. Motoyama, This Bulletin, **31**, 776 (1958).
2) Y. Urushibara, ibid., **25**, 280 (1952).
3) Y. Urushibara and S. Nishimura, ibid., **27**, 480 (1954).
4) Y. Urushibara, S. Nishimura and H. Uehara, ibid., **28**, 446 (1955).
5) S. Nishimura, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **78**, 1741 (1957).

has been investigated since 1954. During the successive investigations it was noticed that this catalyst could not hydrogenate aromatic compounds such as benzene, aniline, etc., even under severe conditions, although it was very effective for the hydrogenation of ethylenic compounds, aldehydes, ketones, nitro compounds, oximes, nitriles and simple phenols[6-9]. To get rid of this defect, an attempt was made to prepare a new type of Urushibara catalyst from nickel chloride and aluminum instead of zinc. Some information on the new Urushibara catalyst thus obtained, named Urushibara nickel BA or U-Ni-BA in abbreviation, was reported briefly in the preceding paper[1].

In the present paper, the hydrogenation of several aromatic compounds with this new catalyst and certain useful modifications of procedure for the preparation of this new catalyst are described.

Hydrogenation of Aromatic Compounds

The Urushibara nickel BA was found to be effective for the hydrogenation of aromatic nucleus which had not been hydrogenated with U-Ni-B or U-Ni-A. The results of the hydrogenation of some aromatic compounds are summarized in Table I. The hydrogenation of phenol can also be attained with either U-Ni-B or U-Ni-A, but it takes much time to complete the reaction with these catalysts even under considerable high temperature. With U-Ni-BA, however, phenol can be easily hydrogenated at lower temperature. It is evident from these results that the U-Ni-BA has a high activity for the hydrogenation of aromatic nucleus, and that the use of aluminum grains instead of zinc dust brings about a favorable change on the property of Urushibara catalyst. It is obvious that the difference between the properties of these two kinds of Urushibara catalysts is due to the difference of the metal combined with nickel in each catalyst.

Preservability of Urushibara Catalyst

Preparation of catalyst has been generally thought to be troublesome and difficult, but it is not true for the preparation of Urushibara nickel catalyst, because it is prepared by simple operations in only an hour or less. However, the preparation of U-Ni-BA from nickel chloride and aluminum grains requires somewhat longer time than that of the other Urushibara catalysts from nickel chloride and zinc dust. A certain useful modification has been made in the procedure for the

TABLE I. HYDROGENATION OF ORGANIC COMPOUNDS

Catalyst: U-Ni-BA containing about 2 g. of nickel,
Sample: 10 g., Solvent: 99% ethanol 50 cc.

Sample	mol.	Initial pressure atm.	Temp. °C	Time hr.	Hydrogen absorbed mol.	Products & Yield* %
Phenol	0.106	66	70~110	1.0	0.355	Cyclohexanol (79)
Methyl salicylate	0.066	65	84~115	2.0	0.190	Ethyl hexahydrosalicylate** (65)
Ethyl benzoate	0.066	54	106~150	2.5	0.231	Ethyl hexahydrobenzoate (82)
Diethyl phthalate	0.045	68	114~154	3.0	0.145	Diethyl hexahydrophthalate (91)
Benzene	0.128	100	100~142	3.0	0.403	Cyclohexane (70)
Ethylbenzene	0.094	70	100~143	4.0	0.308	Ethylcyclohexane (63)
Aniline	0.108	96	150~209	3.5	0.334	*N*-Ethylcyclohexylamine*** (71) Dicyclohexylamine
Acetanilide	0.074	75	120~206	5.0	0.236	Hexahydroacetanilide (77)

* Increased yields may be obtained in case of large scale operations.
** Ester exchange was observed during hydrogenation, and yet the product was found to contain an appreciable amount of methyl ester.
*** *N*-Ethylation was observed during hydrogenation (cf. H. I. Cramer et al., Ref. 10)

6) K. Hata et al., ibid., **77**, 1405 (1956).
7) K. Hata, S. Taira and T. Higase, ibid., **78**, 186 (1957).
8) I. Motoyama, ibid., **79**, 1296 (1958).
9) K. Hata, S. Taira and Y. Satomi, ibid., **79**, 1298 (1958).
10) H. I. Cramer and H. Adkins, *J. Am. Chem. Soc.*, **52**, 4354 (1930).

TABLE II. HYDROGENATION OF PHENOL TO CYCLOHEXANOL
Catalyst: U-Ni-BA (2 g. Ni), Sample: phenol 10 g.,
Solvent: ethanol 50 cc. A small amount of NaOH was added.

Solvent for preservation	Period of preservation day	Initial pressure atm.	Temp. °C	Time hr.	Hydrogen absorbed l. at 20 °C, 1 atm.	Isolated cyclohexanol g.
(Not preserved)	0	66	70~110	1.0	8.6	7.9
Water	6	50	76~117	1.5	7.8	8.5
〃	90	75	79~120	1.5	8.0	8.2
Ethanol	6	50	68~119	1.5	7.6	8.3
〃	90	77	74~120	1.7	7.9	7.9
None (dry)	1	65	66~112	1.5	7.5	7.7
〃	15	82	70~120	1.3	7.9	6.3
					(calcd. 7.7	10.6)

TABLE III. HYDROGENATION OF ORGANIC COMPOUNDS
Catalyst: U-Ni-BA (2 g. Ni) prepared from the precipitated nickel preserved in dry state.

Sample	mol.	Solvent	Initial pressure atm.	Temp. °C	Time hr.	Products & Yield %
Benzene	0.27	None	80	90~150	2.5	Cyclohexane (77)
Aniline	0.11	Ethanol	75	150~208	3.0	*N*-Ethylcyclohexylamine (69) Dicyclohexylamine
Aniline	0.11	Cyclohexane	70	150~215	3.0	Cyclohexylamine (35) Dicyclohexylamine (38)
Pyridine	0.10	Cyclohexane	65	150~218	3.0	Piperidine (86)

preparation of U-Ni-BA catalyst, so as to shorten the time required for the preparation. The principle of the modification is to prepare the U-Ni-BA catalyst from preserved nickel precipitate, which is previously made in large quantities. After the ion-exchange reaction between nickel chloride and aluminum grains, the precipitated nickel is preseved in a proper manner, and then treated with aqueous alkali to make up the U-Ni-BA catalyst when it is used for hydrogenation. Such preservation of the precipitate, however, was expected to cause deactivation of the catalyst, because it is presumed that active nickel surface are inherently present in the precipitate but are covered with certain water-insoluble substances, and consequently the precipitated nickel itself, as it is precipitated, is ineffective as catalyst, unless it is treated with alkali or acid[1].

The activity of the catalyst prepared from the preserved precipitate was examined by the hydrogenation of phenol. The precipitate was preserved from a day to three months in the following three ways: in distilled water, in 99% ethanol and in dry state. Each preserved precipitate was then treated with 20% aqueous sodium hydroxide solution to prepare the catalyst. The results of the hydrogenation of phenol are summarized in Table II. As shown in Table II, each 3 mol. of hydrogen were absorbed with the catalyst prepared from the preserved precipitate as well as with that immediately treated with alkali after the ion-exchange reaction, although the time required for hydrogenation was somewhat longer with the former catalyst. About 8 g. of cyclohexanol were isolated similarly from every reaction mixture. Thus, contrary to expectation, no remarkable deactivation was found with U-Ni-BA catalyst by any preservation of the precipitated nickel. The precipitate preserved in dry state is more convenient for use than those preserved in water or ethanol.

When the dried precipitate is exposed to air under ordinary pressure, it is rapidly oxidized generating a considerable amount of heat. Therefore, it is desirable to keep it under reduced pressure, especially in case of a large scale operation.

Additional results of the hydrogenation with the catalyst prepared in this way are summarized in Table III. It can be seen from these results that this catalyst still maintains the similar catalytic activity as the catalyst prepared from precipitated

TABLE IV. PHYSICAL CONSTANTS OF THE PRODUCTS

Compound	b. p. °C/mmHg.	Refractive index (°C)	Derivative (m.p., °C)
Cyclohexanol	157~162		3,5-Dinitrobenzoate (112)
Ethyl hexahydrosalicylate	115~119/19	1.4674(16.0)	
Ethyl hexahydrobenzoate	87~88/20~21	1.4437(22.0)	Amide (183~187)
Diethyl hexahydrophthalate	145.5/20	1.4523(22.0)	Free acid (197~198)
Cyclohexane	78~ 80	1.4315(23.0)	
Ethylcyclohexane	125~132	1.4315(27.5)	
N-Ethylcyclohexylamine	160~167		Hydrochloride (183~185)
Cyclohexylamine	130~136	1.4673(13.5)	*N*-Acetyl (104~105)
Dicyclohexylamine			Hydrochloride (above 210) (Found: N, 6.56%)
Hexahydroacetanilide	103~104 (m. p.)		
Piperidine			*N*-Benzenesulfonyl (93.5)

nickel immediately after the ion-exchange reaction (cf. Table I).

It is quite interesting that the U-Ni-BA catalyst prepared from the precipitated nickel being kept in air for a long time maintains its high catalytic activity for the hydrogenation of aromatic compounds.

The modification in this way can be applied not only to the new Urushibara catalyst but also to the old ones.

Experimental

Apparatus.—Hydrogenation was carried out in an autoclave of stainless steel with a magnetic stirrer (capacity: 200 cc., rate of stirring: about 60 strokes per min.).

Catalyst.—Catalyst was prepared according to the procedure previously reported[1] and washed thrice with 99% ethanol, when the hydrogenation was carried out in ethanol. When another solvent was employed, the catalyst was washed first thrice with 99% ethanol and then thrice with the solvent.

Preservation in Dry State.—The precipitate, obtained from 100 ml. of aqueous nickel chloride solution containing 40 g. of $NiCl_2 \cdot 6H_2O$ and 50 g. of aluminum grains (40~80 meshes), was washed well with distilled water, then collected on Büchner funnel and dried under reduced pressure. Final weight of the precipitate was about 70 g.* in all. Each 14 g. of the dry precipitate, which contains 2 g. of nickel, was treated with 250 g. of 20% aqueous sodium hydroxide solution before the application for hydrogenation.

Materials.—All substances used for hydrogenation were purified by redistillation or recrystallization except those with special indication.

Methyl salicylate, ethyl benzoate and diethyl phthalate were respectively prepared by usual esterification[11] from corresponding acids.

Benzene was purified by treatment first twice with anhydrous aluminum chloride[12], then with a large amount of U-Ni-A[13]. The purified benzene was redistilled before hydrogenation.

Products.—Reduction products were fractionally distilled except those with special indication, and were identified through appropriate derivatives. When the products were liquid, their refractive indices were measured. Physical constants of the products are summarized in Table IV.

Cyclohexane and ethylcyclohexane were respectively separated from the solvent by adding a large quantity of water to the reaction mixture, dried over anhydrous calcium chloride and distilled.

Piperidine was converted to its hydrochloride by adding an excess of concentrated hydrochloric acid to the reaction mixture after removal of catalyst. The solvent was distilled off and the residue was completely dried up under reduced pressure. Then, the resulting piperidine hydrochloride was purified by recrystallization from 99% ethanol.

Summary

A new Urushibara nickel catalyst, U-Ni-BA, was prepared from nickel chloride and aluminum grains. This new catalyst was found to be highly active for the hydrogenation of aromatic nucleus, contrary to the older Urushibara nickel catalyst, U-Ni-A or U-Ni-B.

The preservability of the catalyst was examined: the precipitate, obtained by the reaction of nickel chloride with aluminum grains (or zinc dust), was kept for a long time in solvent or in dry state, and a similarly active catalyst could be obtained by digesting the preserved precipitate with aqueous caustic alkali.

The author wishes to express his hearty thanks to Professor K. Hata for his kind guidance and valuable suggestion throughout the course of this study, and to Mr.

* This weight varies with experimental condition.

11) E. Fischer and A. Speier, *Ber.*, **28**, 3253 (1895).

12) R. J. Graul and J. V. Karabinos, *Science*, **104**, 557 (1946).

13) H. N. Holmes and N. Beeman, *Ind. Eng. Chem.*, **26**, 172 (1934).

S. Taira for his useful advice. The cost of this investigation was defrayed from the Scientific Research Expenditure of the Minstiry of Education.

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An Approximate Method of Calculating Localization Energies in Alternant Hydrocarbons

By Hiroaki BABA

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Since the localization theory was first proposed by Wheland[1], it has been one of the most effective means of dealing with the chemical reactivity in conjugated organic compounds. The only fault found with this theory is that the calculation of localization energies is frequently an arduous task, especially when one is treating a large molecule. By taking into consideration the characteristic property of nonbonding molecular orbitals, Dewar[2] developed a convenient method of obtaining approximate values of localization energies for alternant hydrocarbons, and successfully applied it to some organic reactions[3]. However, the values obtained by this method of approximation are in general numerically far from being the exact values.

In a previous paper[4] it was made clear that in an alternant hydrocarbon the exact value of localization energy has an intimate correlation with Dewar's approximate one, and also with the value of free valence, the latter quantity being an important index of chemical reactivity[5]. In connection with this problem, another approximate method of computing localization energies in alternant hydrocarbons will be described in the present article.

Definition

The present treatment is based on the simple LCAO molecular orbital method with neglect of overlap integrals; the notation is the same as that used in the preceding papers[4,6].

Consider a carbon atom r in an alternant hydrocarbon, and denote the carbon atoms adjacent to atom r by t, t', ……. Suppose that β_{rt}, $\beta_{rt'}$, …… simultaneously change from their initial value β to a certain value β_r, and that the other coulomb and resonance integrals remain unchanged. Then, bond number N_r can be regarded as a continuous function of β_r. If this function is represented by $N_r(\beta_r)$, the localization energy of atom r is expressed as[4]

$$L^{(r)}=\int_{\beta}^{0}2N_r(\beta_r)\mathrm{d}\beta_r. \tag{1}$$

Next, reference will be made to two known approximate values[4] of $L^{(r)}$. One is

$$L^{(r)\prime}=-2N_r^0\beta \tag{2}$$

where $N_r^0[\equiv N_r(\beta)]$ is the bond number in the initial state, and is connected with free valence F_r^0 by the relation $N_r^0=\sqrt{3}-F_r^0$. The other is

$$L^{(r)\prime\prime}=-2N_r(0)\beta \tag{3}$$

where

$$N_r(0)=\lim_{\beta_r\to 0}N_r(\beta_r)$$

As was proved in the previous paper[4], $L^{(r)\prime\prime}$ defined by Eq. 3 agrees with Dewar's approximate value mentioned in the introductory paragraph.

In the simple molecular orbital procedure, the total energy for the ground state of a system of electrons is obtained as the sum of the energies of the ground-state molecular orbitals to which the individual electrons belong. If the orbital energies are determined by the usual variation method, the total energy obtained in this way corresponds to its absolute minimum under the restriction that the orbitals form

1) G. W. Wheland, *J. Am. Chem. Soc.*, **64**, 900 (1942).
2) M. J. S. Dewar, ibid., **74**, 3357 (1952).
3) P. M. G. Bavin and M. J. S. Dewar, *J. Chem. Soc.*, **1956**, 164; M. J. S. Dewar, T. Mole and E. W. T. Warford, ibid., **1956**, 3581, and related papers.
4) H. Baba, This Bulletin, **30**, 154 (1957).
5) See, for instance, B. Pullman and A. Pullman, "Progress in Organic Chemistry", Vol. 4, edited by J. W. Cook, Butterworths Scientific Publications, London (1958), pp. 31—71.
6) H. Baba, This Bulletin, **30**, 147 (1957).

an orthonormal set. If one keeps this fact in mind, it is easily verified that N_r decreases monotonously as β_r increases. Hence

$$N_r^0 > N_r(\beta_r) > N_r(0) \quad (\beta < \beta_r < 0) \tag{4}$$

so that from Eqs. 1—3

$$L^{(r)\prime} > L^{(r)} > L^{(r)\prime\prime} \tag{5}$$

Let us now consider a new quantity $\boldsymbol{L}^{(r)}$ defined as follows:

$$\boldsymbol{L}^{(r)} = -(N_r^0 + N_r(0))\beta \tag{6}$$

Then, from Eqs. 2 and 3

$$\boldsymbol{L}^{(r)} = \frac{1}{2}(L^{(r)\prime} + L^{(r)\prime\prime}) \tag{7}$$

Since both $L^{(r)\prime}$ and $L^{(r)\prime\prime}$ are approximate values of $L^{(r)}$, $\boldsymbol{L}^{(r)}$ will also be an approximation of $L^{(r)}$.

The relation of $\boldsymbol{L}^{(r)}$ with other quantities may be understood by Fig. 1, where the full line curve aeb represents the relation between β_r and $2N_r(\beta_r)$. $L^{(r)}$ is, of course, equal to the area under the curve, $L^{(r)\prime}$ to the area of rectangle agcd, and $L^{(r)\prime\prime}$ to that of rectangle hbcd, while $\boldsymbol{L}^{(r)}$ is equal to the area of trapezoid afbcd.

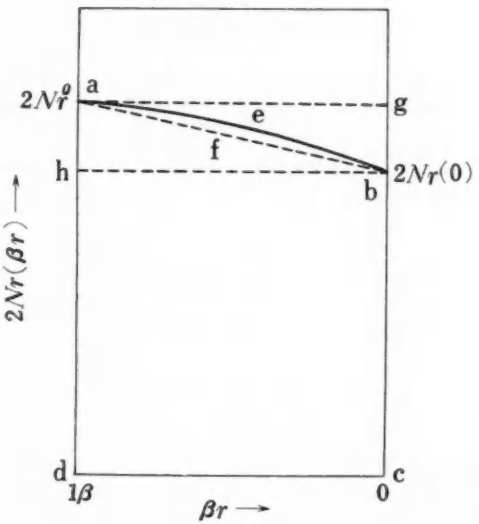

Fig. 1.

Examples and Discussion

In Table I are listed the values of $\boldsymbol{L}^{(r)}$ and other related quantities for three positions of anthracene. In Fig. 2 $\boldsymbol{L}^{(r)}$, $L^{(r)\prime}$ and $L^{(r)\prime\prime}$ are plotted against $L^{(r)}$ for a number of alternant hydrocarbons. The values of $L^{(r)}$ for primary, secondary and tertiary carbon atoms fall within the ranges 1.0 to 1.8, 1.8 to 2.6 and 2.6 to 3.1, respectively. The examples presented in this table and figure clearly show that $\boldsymbol{L}^{(r)}$ is superior to $L^{(r)\prime}$ and $L^{(r)\prime\prime}$ as an approximation of $L^{(r)}$.

TABLE I. LOCALIZATION ENERGIES IN UNITS OF $-\beta$ FOR ANTHRACENE

Position	$L^{(r)}$	$\boldsymbol{L}^{(r)}$	$L^{(r)\prime}$	$L^{(r)\prime\prime}$
1	2.25	2.06	2.55	1.57
2	2.40	2.27	2.65	1.89
9	2.01	1.84	2.42	1.26

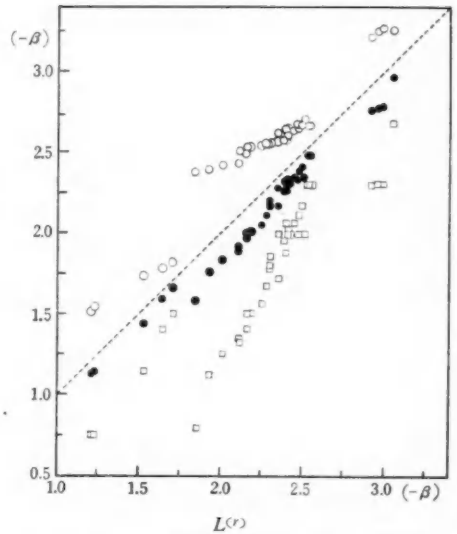

Fig. 2. Relations between $L^{(r)}$ and $\boldsymbol{L}^{(r)}$, $L^{(r)\prime}$ and $L^{(r)\prime\prime}$.
●, $\boldsymbol{L}^{(r)}$; ○, $L^{(r)\prime}$; □, $L^{(r)\prime\prime}$.
$L^{(r)}$ and $L^{(r)\prime}$: Taken from references 5 and 6, and "Dictionary of Values of Molecular Constants", Vol. II, edited by C. A. Coulson and R. Daudel.
$L^{(r)\prime\prime}$: Taken from reference 2, and calculated by the present author.

Previously it was shown by the present author[4,6] and also by Fukui et al.[7] that under certain conditions there is a definite parallelism among the quantum mechanical quantities, including $L^{(r)\prime}$ and $L^{(r)\prime\prime}$, which are related to the reactivity of an alternant hydrocarbon. Considering the definition of $\boldsymbol{L}^{(r)}$, one may at once reach the conclusion that the same parallelism exists between $\boldsymbol{L}^{(r)}$ and any other quantity mentioned above.

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7) K. Fukui, T. Yonezawa and C. Nagata, *J. Chem. Phys.*, **26**, 831 (1957).

Tropones. IV. Ultraviolet Absorption Spectra of Reaction Products of Tropones and Carbonyl Reagents***

By Toshio MUKAI

(Received June 8, 1959)

The reaction products of tropone and carbonyl reagents, such as oxime, semicarbazone, thiosemicarbazone, phenylhydrazone, and nitrophenylhydrazone form peculiar conjugation systems and they are of interest in the study of ultraviolet spectrum. These compounds generally have deep color, ranging from orange to dusky purple. The present paper describes observations on the ultraviolet spectra of products obtained on the reaction of tropone and tropones possessing the methyl, phenyl, naphthyl, *o*-tolyl, or benzyl group in 2-position, and carbonyl reagents, measured in methanol, acidic and alkaline solutions.

The ultraviolet spectrum of tropone oxime[1], of tropone semicarbazone[1] and of tropone thiosemicarbazone are shown in Figs. 1–3, respectively. These three compounds possess a C=N– group in place of the carbonyl group in tropone and show two typical absorption maxima as tropone itself does[1]. The maximum absorption in methanol solution shifts to longer wavelengths in the order of the oxime, semicarbazone and thiosemicarbazone, and this tendency is the same as that in the case of unsaturated ketone derivaives in general[2]. All three compounds have fairly deep color which must be due to the broad absorption appearing at the wavelength region above 400 mμ.

The ultraviolet spectra of the oxime and semicarbazone in hydrochloric acid solution show a shift to a longer wavelength region and that of the thiosemicarbazone to slightly shorter wavelengths. The absorption maxima lie near 240 and 330 mμ in all three compounds and the value of their intensity is also similar.

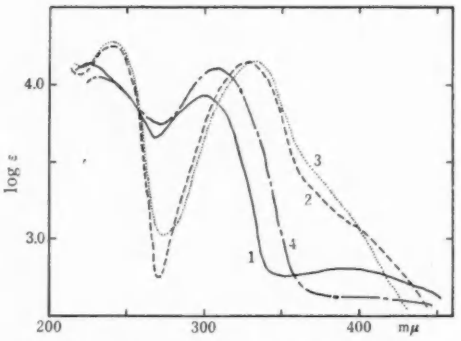


Fig. 1. Ultraviolet absorption spectra of tropone oxime: (1) in methanol, (2) in 0.1 N HCl, (3) in 6 N HCl and (4) in 0.1 N NaOH solution.

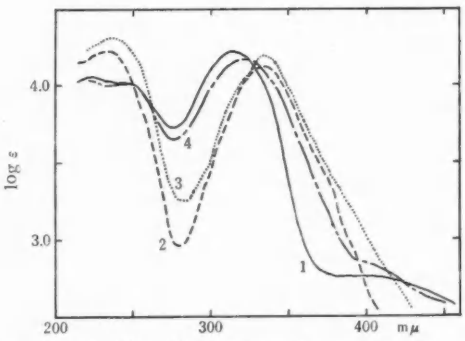


Fig. 2. Ultraviolet absorption spectra of semicarbazone of tropone: (1) in methanol, (2) in 0.1 N HCl, (3) in 6 N HCl and (4) in 0.1N NaOH solution.

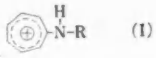
This fact indicates that they all have a structure of conjugate acid like I and that their absorptions are not so greatly affected by group R. The fact that there is no shift of the absorption curve according to the concentration of hydrocholric acid (in 0.1 or 6 N), suggests that the formation of the conjugate acid (I) is almost complete even in dilute acid solution such as 0.1 N solution.

* Part I: Ref. 1; Part II: T. Mukai, This Bulletin, **31**, 846 (1958); Part III: Ref. 3.

** Presented before the 39th Tohoku Local Meeting of the Chemical Socity of Japan, Sendai, May, 1956.

1) T. Nozoe, T. Mukai and T. Takase, *Sci. Repts. Tohoku Univ., First Ser.*, **39**, 164 (1956).

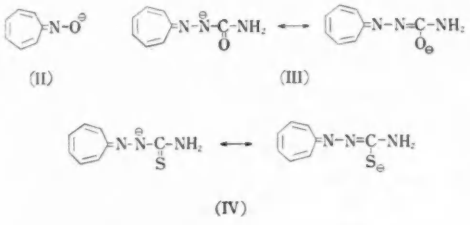
2) A. E. Gillam and E. S. Stern, "An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry", Edward Arnold Publishers, Ltd., London (1955), p. 100.



(I)

R=OH, $NHCONH_2$, $NHCSNH_2$

In alkaline solution, the absorption curves of the oxime, semicarbazone and thiosemicarbazone, all show a shift to a longer wavelength region. It has already been pointed out that the oxime has an amphoteric property, is stable, and dissolves both in acids and in alkalis[1], and this shift is assumed to be due to the formation of an anion (II). Similarly, formation of anions (III) and (IV) can be expected for the semicarbazone and thiosemicarbazone.



(II) (III)

(IV)

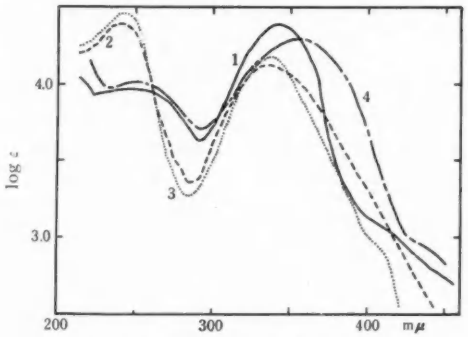


Fig. 3. Ultraviolet absorption spectra of thiosemicarbazone of tropone: (1) in methanol, (2) in 0.1 N HCl, (3) in 6 N HCl and (4) in 0.1N NaOH solution.

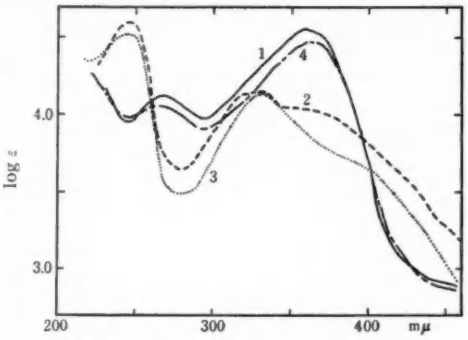


Fig. 4. Ultraviolet absorption spectra of *p*-bromophenylhydrazone of tropone: (1) in methanol, (2) in 0.1 N HCl (3) in 6 N HCl and (4) in 0.1 N NaOH solution.

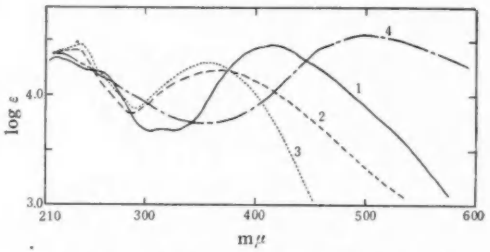


Fig. 5. Ultraviolet absorption spectra of 2,4-dinitrophenylhydrazone of tropone: (1) in methanol, (2) in 0.1 N HCl, (3) in 6 N HCl and (4) in 0.1 N NaOH solution.

Ultraviolet absorption spectra of the phenylhydrazone[1] and *p*-bromophenylhydrazone[1] of tropone are shown in Table I and Fig. 4 and those of *p*-nitrophenylhydrazone[1] and 2,4-dinitrophenylhydrazone[1] of tropone in Table I and Fig. 5. These phenylhydrazones exhibit absorption maximum at a longer wavelength region than the oxime and semicarbazone do. Further it is seen that the introduction of a nitro group in the

TABLE I. ABSORPTION MAXIMA OF TROPONE DERIVATIVES IN mμ (log ε)

	MeOH	0.1 N HCl	6 N HCl	0.1 N NaOH
Phenylhydrazone	256(4.11)	240(4.41)		252(3.97)
	355(4.43)	328(4.05)		355(4.33)
p-Nitrophenylhydrazone	255(inf)	237(4.42)	237(4.42)	255(sh)
	315(3.78)	356(4.40)	350(4.27)	303(3.83)
	383(3.83)			510(4.27)
	429(4.55)			
2,4-Dinitrophenylhydrazone	219(4.34)	237(4.40)	238(4.45)	220(sh)
	260(4.20)	363(4.23)	353(4.29)	500(4.53)
	315(3.70)			
	413(4.45)			

TABLE II. ABSORPTION MAXIMA OF OXIMES IN mμ (log ε)

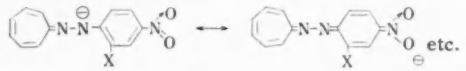
	MeOH	0.1 N HCl	6 N HCl	0.1 N NaOH
2-Methyltropone	228(4.24)	243(4.31)	243(4.36)	236(4.16)
	300(3.85)	338(4.09)	338(4.11)	303(3.90)
	360(2.91)*			
	390(2.91)*			
2-Phenyltropone	222(4.20)	237(4.23)	238(4.33)	235(4.14)
	260(4.04)	345(3.95)	341(4.06)	265(4.05)
	307(3.75)			308(3.70)
2-Benzyltropone	228(4.21)	240(4.27)	243(4.35)	243(4.15)
	300(3.78)	339(3.98)	340(4.11)	303(3.85)
	358(2.93)*			
	380(2.93)*			
2-α-Naphthyltropone	222(4.89)	222(4.92)	224(4.86)	223(4.84)
	293(4.04)	240(4.28)	245(4.30)	297(3.97)
	380(3.17)*	280(3.83)	334(3.99)	
		336(4.01)		
2-o-Tolyltropone	295(3.82)	240(4.27)	240(4.37)	238(4.21)
	ca. 355(3.10)*	340(4.00)	339(4.11)	308(3.90)

* Broad band. These bands can not be compared with each other.

ortho- or para-position of the phenyl ring results in a further shift of the maximum to a longer wavelengths (above 400 mμ).

In hydrochloric acid solution, they all show a shift originating in the formation of a conjugate acid [I: R= $-NH-C_6H_5$, $-NH-C_6H_4Br(p)$, $-NH-C_6H_4NO_2(p)$, $-NH-C_6H_3(NO_2)_2(2,4)$]. In *p*-nitro- and 2,4-dinitrophenylhydrazones, there is a shift of 6~10 mμ when the concentration changes from 0.1 to 6 N hydrocholric acid. This is probably due to the weakened basicity of these compounds by the introduction of a nitro group which has an effect on the formation of the conjugate acid (I).

In alkaline solution, the absorption maxima of *p*-nitro and 2,4-dinitrophenylhydrazone shift to a longer wavelength region (above 500 mμ) and this is due to the formation of an anion (V) with a long chain of conjugation. The formation of an anion (V) is supported by the fact that phenylhydrazone and *p*-bromophenylhydrazone hardly show any shift in alkaline solution (see Fig. 4).



(V) X=H, NO_2

The ultraviolet absorption spectra of *p*-nitrophenylhydrazone in methanol and alkaline solution exhibit maxima at somewhat longer wavelength than that of 2,4-dinitrophenylhydrazone and this is due to the steric hindrance of the nitro group in 2-position of the phenyl ring. However, the maximum of 2,4-dinitrophenylhydrazone appears in a longer wavelength than that of *p*-nitrophenylhydrazone in acid solution. This is probably due to the fact that resonance represented by V occurs only to a small extent in acid solution and consequently the interference of the nitro group in 2-position of the phenyl group does not give an effect on the spectrum.

Of these products from reaction with carbonyl reagents, oxime and 2,4-dinitrophenylhydrazone are easily formed in tropones possessing alkyl or aryl radical in its 2-position. Effect of a substituent on the ultraviolet spectrum was examined with oximes. Ultraviolet spectra of oximes are shown in Table II.

The absorption maxima of 2-methyltropone oxime[3] in longer wavelength region shift to a slightly shorter wavelengths than those of tropone oxime when measured in methanol or 0.1 N sodium hydroxide solution but conversely shift to a longer wavelength in hydrochloric acid solution. Of these oximes, the interesting thing is the absorption of 2-phenyltropone oxime[4]. As will be seen from Fig. 6, the curve appears different since new absorption maxima appear at

3) T. Mukai, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **79**, 1547 (1958),

4) T. Nozoe, T. Mukai, J. Minegishi and T. Fujisawa, *Sci. Repts. Tohoku Univ., First Ser.*, **37**, 388 (1954).

TABLE III. ABSORPTION MAXIMA OF 2,4-DINITROPHENYLHYDRAZONE IN mμ (log ε)

	MeOH	0.1 N HCl	6 N HCl	0.1 N NaOH
2-Methyltropone	222(4.36)	239(4.44)	243(4.56)	491(4.40)
	317(3.65)	391(4.24)	354(4.36)	
	410(4.43)			
2-Phenyltropone	232(4.43)	228(4.20)	238(4.25)	ca. 250(4.20)
	405(4.44)	257(4.08)	363(4.05)	498(4.30)
		403(4.12)		
2-Benzyltropone	260(4.17)	410(4.35)	243(4.43)	255(4.30)
	411(4.36)		358(4.23)	490(4.45)
2-α-Naphthyltropone	222(4.97)	222(4.96)	222(4.93)	223(4.94)
	260(4.28)	406(4.32)	241(4.50)	490(4.37)
	410(4.38)		355(4.30)	
2-o-Tolyltropone	260(4.26)	240(4.41)	242(4.51)	480(4.17)
	408(4.42)	401(4.33)	358(4.32)	

260 and 265 mμ in methanol and alkali solution. It is considered that the absorption in this region is due to the coplanarity of the seven-membered ring and phenyl ring, as in the case of 2-phenyltropone itself[5,7].

On the other hand, the absorption of 2-benzyltropone oxime[5] is very similar to that of 2-methyltropone by the introduction of a methylene group, while the absorption of 2-α-naphthyltropone oxime does not exhibit the maximum at around 260 mμ seen in the case of 2-phenyltropone oxime, irrespective of the presence of the naphthyl group. Moreover, the second absorption maximum of 2-naphthyltropone oxime have shifted to a shorter wavelength region than the corresponding absorption maximum of 2-phenyltropone oxime in methanol solution (Table II) and a steric interference between the tropone ring and the naphthyl group at peri-position may be considered at its cause. The absorption maximum at 222~224 mμ of strong intensity seen in 2-α-naphthyltropone oxime is thought to be the absorption of naphthalene itself[8]. The ultraviolet spectrum of 2-o-tolyltropone oxime[5] also suggests the presence of a steric hindrance by the methyl group in the ortho-position of the phenyl ring. Owing to this effect, this compound has a maximum at 295 mμ which is considerably shifted toward shorter wavelength compared with a maximum of phenyltropone oxime at 307 mμ.

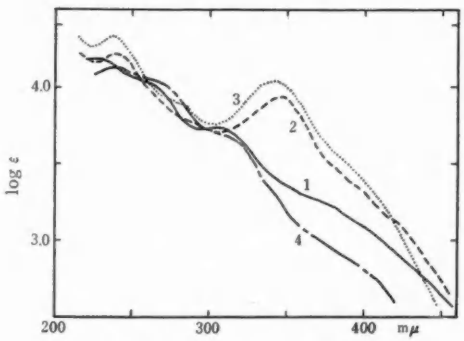


Fig. 6. Ultraviolet absorption spectra of oxime of 2-phenyltropone: (1) in methanol, (2) in 0.1 N HCl, (3) in 6 N HCl and (4) in 0.1 N NaOH solution.

Ultaviolet absorption spectra of 2,4-dinitrophenylhydrazones of various tropones are shown in Table III. In these cases also, the direction of the shift in hydrochloric acid and alkali solutions are the same as in the case of 2,4-dinitrophenylhydrazone of tropone, but the relationship between the shift of absorption and kind of substituents is complicated and conclusive explanation is difficult. The marked tendency of these is the small of shift in the absorption of 2-phenyl-, 2-benzyl- and 2-α-naphthyl-tropone derivatives measured in 0.1 N hydrochloric acid solution. The reason for this is the smallness in basicity and it may be considered that the stronger the basicity, the larger will be the shift. In 6 N hydrochloric acid solution, all the compounds

5) T. Nozoe, T. Mukai and I. Murata, *Proc. Japan Acad.*, **29**, 169 (1953).
6) K. Kikuchi, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **77**, 1439 (1956).
7) R. D. Haworth and P. B. Tinker, *J. Chem. Soc.*, **1955**, 911.
8) A. E. Gillam and E. S. Stern, "An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry", Edward Arnold Publishers. Ltd., Londno (1955), p. 122.

have absorption maximum at about 360 mμ and formation of conjugate acids of similar structure may, therefore, be assumed. The absorption maximum of 2-α-naphthyltropone derivative at 222~223 mμ of strong intensity is that of naphthalene itself[5], as was stated earlier.

The author takes this opportunity to express his sincere gratitude Professor Tetsuo Nozoe for his kind guidance throughout the course of this work, and to Professor Shuichi Seto and Assistant Professor Yoshio Kitahara for much helpful advice.

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Geometrical Isomers of α-Stilbazole

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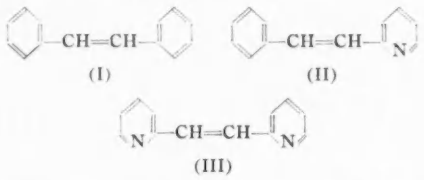
There is a series of stilbene derivatives which are substituted by one or two α-pyridyl groups for the phenyl groups of the stilbene. They are stilbene (I), α-stilbazole (II) and α-pyridostilbene, i.e. 1-2-bis-(α-pyridyl)-ethylene (III).



(I) (II) (III)

They are expected to exist in *cis*- and *trans*-structures as they are all 1,2-disubstituted ethylenes. Among the six isomers, *cis*- and *trans*-stilbene (I) are well known and recently the author reported two geometrical isomers of α-pyridostilbene (III)[1]. However, regarding α-stilbazole hitherto only one species which melts at 91°C has been known to us.

The author presumed that in the course of the preparation of the known species of α-stilbazole, the other isomer would be prepared as one of the by-products and then removed in some processes. The course was re-examined and it was found that the last recrystallization process removed completely the other isomer from the main product. Now, he has recovered the other isomer from the the filtrate, and then determined that the known species of α-stilbazole is a *trans*-isomer and the other is a *cis*-isomer on the basis of the data of the elementary analyses, the melting points, the ultraviolet and the infrared spectra.

Experimental

Syntheses of *cis*- & *trans*-α-Stilbazole.—A mixture of freshly purified benzaldehyde (b.p. 179~180°C), α-picoline (b.p. 129.3°C) and anhydrous zinc chloride in the ratio 3 : 2 : 1 was heated in in an autoclave at 200°C for 24 hr.[2] After being cooled, the dark brown and viscid product was dissolved in aqueous hydrochloric acid, steam distilled to remove benzaldehyde and basified with sodium hydroxide, followed by steam distillation to remove the residual α-picoline. The solution separated raw and purplish red stilbazole, which was extracted with chloroform. The chloroform extract was dried over anhydrous sodium sulfate. After the chloroform was evaporated, the residue was distilled under 10 mmHg pressure. Pale yellow liquid passed over the interval 170~180°C and condensed in a receiver. No α-stilbazole could be found in the fore-run which was collected separately in three traps kept at 0, −20 and −80°C, respectively. The main distillate in the receiver was recrystallized from boiling ethanol. The precipitate (**A**) melts at 91°C and corresponds to the known species of α-stilbazole. The yield was 60% theoretical. After ethanol was evaporated from the filtrate, there remained the brown oil. It was purified repeatedly by the elution chromatography (alumina, 2×40 cm., chloroform) until it showed the constant ultraviolet absorption spectrum. The purified oil (**B**) is colorless and melts at −50.0°C. The yield was nearly 3% theoretical.

Other Materials.—*cis*- & *trans*-*Stilbene.*—*cis*-Stilbene[3] was prepared from *cis*-α-phenylcinnamic

1) T. Katsumoto, This Bulletin, **32**, 1019 (1959).
2) G. H. Lénárt, *Ann.*, **410**, 95 (1915).
3) C. C. Price, "Organic Syntheses", Vol. 33, John Wiley & Sons, Inc., New York (1953), p. 88.

acid and *trans*-stilbene[4] from benzoin, according to the methods of "Organic Syntheses". They were purified by the same method as the above. Their melting and boiling points are shown in Table II.

cis- & trans-α-Pyridostilbene.—The same samples that were synthesized in the preceding experiment[1] were used.

Analyses and Measurements.—Analytical data of the elementary analyses were determined by the Elementary Analyses Center of Kyoto University.

Melting points below the room temperature were measured in the following method, because the samples were so transparent even in the solid state as in the liquid state that the appearances did not change at the melting points. A liquid sample was packed as usual in a capillary tube which was then attached to a thermometer centered in a methanol bath. Dry air was sent into the bath to stir the methanol. A very thin and long glass wire was inserted in the capillary tube. As the bath was cooled in a dry ice-acetone mixture to −70°C, the sample solidified and the glass wire was fixed in it. Then, the methanol bath was transferred to an acetone bath that had been cooled near −40°C. The melting point was clearly observed as the glass wire could not be pulled out until the sample began to melt. *cis*-Stilbene and *cis*-stilbazole were viscid near the melting point.

Boiling points under reduced pressure were measured by Garcia's method[5] as described in the preceding paper[1].

The ultraviolet absorption spectra (in cyclohexane) were made with a Shimadzu QB-50 quartz spectrophotometer. The wavelengths of this photometer were calibrated with the absorption band at 301 mμ of an aqueous potassium nitrate solution. The infrared absorption spectra were obtained with a Hilger or a Leitz spectrophotometer equipped with a rock-salt prism. Readings were taken in the region of 1700~670 cm^{-1} and always calibrated with the absorption bands of polystyrene.

Results and Discussion

As described above, the colorless liquid (**B**) was recovered from the filtrate of the recrystallization of the known species of α-stilbazole (A). The analytical data of the elementary analyses of the liquid (**B**) are shown in Table I and are in good

TABLE I. RESULTS OF THE ELEMENTARY ANALYSES OF **B**

	C	H	N
Found:	85.95%	6.32%	7.93%
Calcd. for $C_{13}H_{11}N$:	86.16	6.12	7.73

TABLE II. THE m.p.'s. AND b.p.'s. OF THE GEOMETRICAL ISOMERS

	Stilbene (I)		α-Stilbazole (II)		α-Pyridostilbene (III)	
	cis	*trans*	**B**(*cis*)	**A**(*trans*)	*cis*	*trans*
m.p.	−54.0°C	125.0°C	−50.0°C	91.0°C	48.5°C	121.0°C
b.p.	142°C/ 10 mmHg		141°C/ 10 mmHg	171°C/ 10 mmHg	149°C/ 15 mmHg	197°C/ 15 mmHg

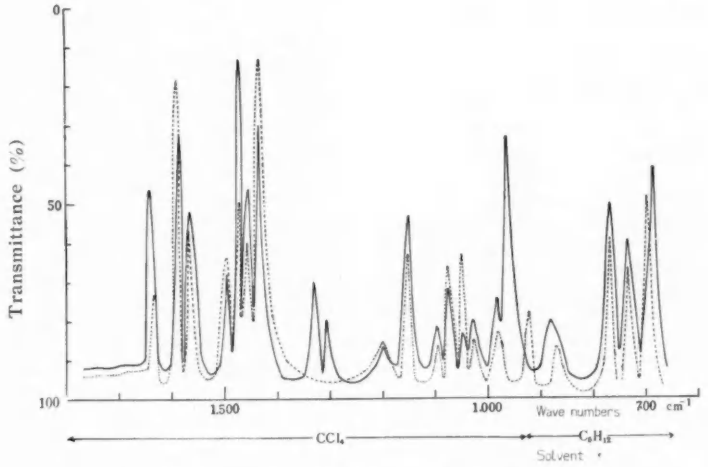


Fig. 1 Infrared absorption spectra of α-stilbazole.
—— **A** (*trans*) ---- **B** (*cis*)

4) L. I. Smith, ibid., Vol. 23 (1943), p. 86.

5) C. Garcia, *Ind. Eng. Chem., Anal. Ed.*, **15**, 648 (1943).

agreement with the calculated values for stilbazole $C_{13}H_{11}N$. It seems that **B** is also a species of α-stilbazole. **B** melts at −50.0°C, which is much lower as compared with the melting point of **A** (91°C). As a *cis*-isomer always melts at much lower temperature than a *trans*-isomer does (Table II and Ref. 6), **A** is a *trans*-isomer and **B** is a *cis*-isomer.

Fig. 1 shows the infrared absorption spectra of **A** and **B** in carbon tetrachloride or in cyclohexane. Each band of **A** is in good agreement with corresponding band of **B**, except two bands at 1330 and 965 cm^{-1} which will be discussed later. The good agreement indicates that **B** is the other isomer of **A**. Furthermore, this determination is made sure by the assignments of these absorption comparing their absorptions with those of the related compounds, stilbene (I) and α-pyridostilbene (III) as shown in Table III.

The fundamental studies[7-9] on benzene vibrations have shown that the characteristic skeletal stretching modes of the semi-unsaturated carbon-carbon bonds lead to the appearance of a group of four bands between 1650~1450 cm^{-1}. Four absorptions corresponding to them are also expected theoretically in the case of pyridine and have been found in the similar range of the spectra of many pyridine derivatives[10,11], although the vibrations are mostly found to shift to somewhat lower frequencies on passing from benzene to pyridine. In these ranges each of **A** and **B** shows seven absorptions due to BR-1, 3, 4 and PR-1, 2, 3, 4 vibration modes (Table III). The letters B and P in the table denote the vibrations arising from a benzene and a pyridine ring, respectively. These spectra show that **A** and **B** each consist of a benzene and a pyridine ring. Randall et al.[12] regarded a bond in the range 1587~1575 cm^{-1}, namely, BR-2 in Table III, as an indication of the conjugation of an ethylenic double bond with an aromatic ring. In the spectra of α-stilbazole the BR-2 vibration is obscure, because the absorption range is very similar to that of the PR-1 vibration and they overlap one another, but the PR-2 vibration corresponding to the BR-2 vibration in the sense of the conjugation, is clearly seen. This shows that a pyridine ring in the α-stilbazole is conjugated with an ethylenic double bond.

In the range 1225~950 cm^{-1}, aromatic compounds all show a series of relatively weak but sharp bands, the positions of which vary with the type of substitution and are independent of the nature of substituents[11]. Randle and Whiffen[13,14] have shown that they arise from the CH in-plane bending modes. Generally, mono-substituted benzenes show three absorptions in the ranges 1175~1125, 1110~1070 and 1070~1000 cm^{-1} [11,14,15]. In the case of α-substituted pyridines the similar absorptions also appear in the ranges 1151~1140, 1050~1040 and 998~986 cm^{-1} [10]. Five absorptions at **A** and **B** are located in the above absorption ranges of the mono-substituted benzenes and the α-substituted pyridines, and correspond to the BHI-2,3 and the PHI-1,2,3 vibration modes. The absorptions due to the BHI-1 seem to be masked with those due to the PHI-1 mode (Table III). These absorptions show that the benzene and the pyridine ring of **A** and **B** are a mono-substituted benzene and an α-substituted pyridine ring.

Mono-substituted benzenes show two strong absorptions in the ranges of 770~730 cm^{-1} [11,12] and 710~690 cm^{-1} [11,12,15]. They are assigned to the out-of-plane CH bending vibrations of five adjacent ring hydrogen atoms remaining on the benzene ring, and the absence of the latter band is a strong evidence of the latter band is a strong evidence of the absence of a mono-substituted benzene. On the other hand, α-substituted pyridines having four adjacent hydrogen atoms on the ring behave like an ortho-substituted benzene and absorb strongly in the range of 780~740 cm^{-1} [10,11]. The three strong bands corresponding to the above bands appear in the spectra of **A** and **B** (BHO-1,2 and PHO in Table III).

Thus, **A** and **B** are both disubstituted ethylenes with a phenyl and an α-pyridyl radical, i.e. α-stilbazole.

Generally, *trans*-ethylenic double bonds give rise to two medium to strong bands in the ranges of 990~965 cm^{-1} [11,16] and 1310

6) M. Murakami, "Organic Stereochemistry (Kōzō Yūki-kagaku)", Asakura Publishers, Tokyo (1956), p. 181.
7) R. C. Lord et al., *J. Chem. Phys.*, **21**, 1170 (1953).
8) F. A. Andersen et al., ibid., **23**, 1047 (1955).
9) F. A. Miller et al., ibid., **24**, 996 (1956).
10) H. Shindo, *Pharm. Bull. (Japan)*, **5**, 472 (1957).
11) L. J. Bellamy, "The Infrared Spectra of Complex Molecules", 2nd Ed., John Wiley & Sons, Inc., New York (1958).
12) H. M. Randall et al., "The Infrared Determination of Organic Structures", van Nostrand, New York (1949).
13) D. H. Whiffen, *J. Chem. Soc.*, **1956**, 1350.
14) D. H. Whiffen et al., *Trans. Faraday Soc.*, **52**, 9 (1956).
15) R. B. Barnes et al., "Infrared Spectroscopy", Reinhold Publishing Corp., New York (1944).
16) R. S. Rasmussen and R. R. Brattain, *J. Chem. Phys.*, **15**, 131, 135 (1947).

TABLE III. INFRARED ABSORPTIONS OF THE THREE PAIRS OF GEOMETRICAL ISOMERS (cm^{-1})

Stilbene(I)		α-Stilbazole (II)			α-Pyridostilbene (III)		Assignment*
cis[a] **	*trans*[b]	**B**(*cis*)[c]	**A** (*trans*)[c]	**A** (*trans*)[b]	*cis*[b]	*trans*[b]	
		1632 m	1643 s	1636 s			
1607 m	1599 m			1598 sh			BR-1
		1590 vs	1586 vvs	1583 vvs	1585 vs	1582 s	PR-1
1578 w	1578 m						BR-2
		1570 s	1565 s	1566 sh	1569 vvs	1567 vs	PR-2
1496 s	1493 vs	1497 s	1497 m	1492 s			BR-3
		1471 s	1471 vvs	1466 vs	1467 vs	1468 vs	PR-3
1455 s	1453 vs	1453 m	1453 s	1453 vs			BR-4
		1435 vs	1433 vs	1428 vs	1438 vvs	1436 vs	PR-4
1412 m					1403 sh		*cis*-EHI
	1333 m		1331 vs	1330 s		1326 s	*trans*-EHI
	1302 m		1307 m	1305 s	1307 m	1303 m	
				1237 m		1234 w	
1183 w		1200 w	1198 w	1198 s			
1158 w	1157 m						BHI-1
		1147 s	1148 s	1147 s	1157 s	1146 s	PHI-1
		1093 w	1095 w	1095 m	1081 m	1090 m	PHI
1077 s	1073 s	1075 m	1074 m	1075 m			BHI-2
		1050 s	1049 w	1053 m	1053 m	1053 m	PHI-2
1033 m	1032 m	1030 w	1030 w	1033 w			BHI-3
		993 w	986 w		994 s	996 sh	PHI-3
	961 vvs		965 vvs	983 vvs		976 vvs	*trans*-EHO
924 s	912 m	923 m					
	880 w		880 w	893 m	893 w	880 m	
864 m	860 w	867 w		868 m			
					786 vs	788 s	
777 vvs	764 vvs	779 vs	772 vvs	779 vvs			BHO-1
		740 vs	735 vs	735 vvs	754 vvs	745 vs	PHO
694 vvs	685 vs	697 vs	688 vs	685 vs			BHO-2
				676 vs			

* BR and PR mean the stretching vibrations of a benzene and a pyridine ring; EHI, BHI and PHI mean the in-plane bending vibrations and EHO, BHO and PHO mean the out-of-plane bending vibrations, of the hydrogen atoms remaining on an ethylene, a benzene and a pyridine ring, respectively.

** The letters, a, b, c, denote the state of the samples in measurements: a, liquid condition without solvent; b, powder in a potassium bromide disk; c, carbon tetrachloride or cyclohexane solution.

TABLE IV. ULTRAVIOLET ABSORPTIONS OF THE THREE PAIRS OF THE GEOMETRICAL ISOMER (IN CYCLOHEXANE)

Compound	*cis*-Form				*trans*-Form			
	E-band		K-band		E-band		K-band	
	λ_{max}, mμ	ε	λ_{max}, mμ	ε	λ_{max}, mμ	ε	λ_{max}, mμ	ε
Stilbene (I)	207	19450	275	10730	228	15900	295	26600
	224	22600					306	24600
α-Stilbazole (II)	220	14860	285	9630	222	10570	275	15620
					228	11130	285	16470
					235	8570	314	24220
α-Pyridostilbene(III)	211	9920	257	5790	221	8770	267	15750
			262	5910	226	6620	316	28470
			268	4420			331	20510

$\sim$1290 cm^{-1} [11]. The former band was assigned by Kilpatrick and Pitzer to the out-of-plane bending vibration[11], while the latter was assigned by Sheppard and Sutherland[17] to the in-plane bending vibration, of the hydrogen atoms remaining on the *trans*-disubstituted ethylene. Especially the absence of the former band can be regarded as the conclusive evidence of the *trans*-ethylenic linkage. Not any absorptions corresponding to the above absorptions are found in the spectrum of **B**, while **A** gives rise to the two strong absorptions at 965 and 1330 cm^{-1} due to the *trans*-substituted ethylene (EHO, EHI in Table III). Thus, **B** is *cis*-α-stilbazole and **A** is *trans*-α-stibazole.

The ultraviolet spectra of **A** and **B** are compared with those of *cis*- and *trans*-isomers of stilbene (I) and α-pyridostilbene (III) in Table IV and Figs. 2-4. Each spectrum of stilbene and α-pyridostilbene consists of the E(ethylenic)-band and the K(conjugated)-band (Figs. 2 and 3). All the E-bands of both *cis*- and trans-isomers lie near 220 mμ. However, every K-band of the *trans*-isomer lies at a longer wavelength than that of the *cis*-isomer does. In addition, the intensity of the K-band is always much stronger in the *trans*-isomer than in the *cis*-isomer. The bathochromic displacements and much increase of the absorption intensities arise from the coplanarity of the molecular structure and then from the high degree of resonance on passing from the *cis*-structure to the

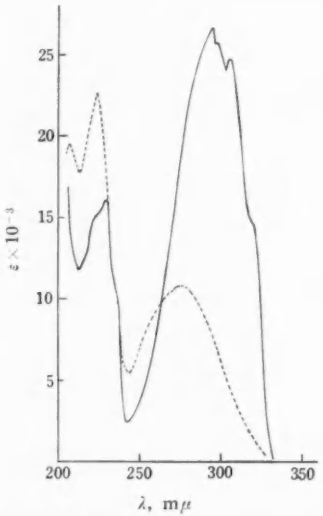


Fig. 2. Ultraviolet absorption spectra of stilbene.
—— *trans*-Fom - - - - *cis*-Form

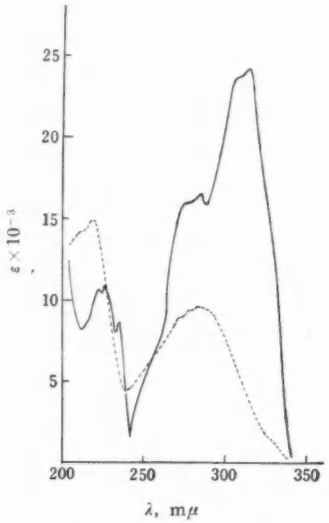


Fig. 3. Ultraviolet absorption spectra of α-stilbazole.
—— **A** (*trans*) - - - - **B** (*cis*)

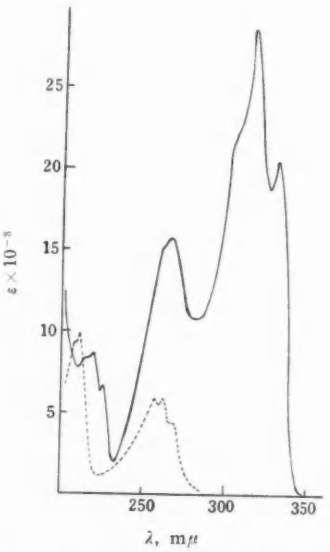


Fig. 4. Ultraviolet absorption spectra of α-pyridostilbene.
—— *trans*-Form - - - - *cis*-Form

17) N. Sheppard and G. Sutherland, *Proc. Roy. Soc.*, **A196**, 195 (1949).

trans-structure[18]. Robertson and Woodward[19] indicated that, as the results of X-ray diffraction measurements, in *trans*-stilbene the bond joining the phenyl groups to the ethylenic group are 1.45 Å long. As the bond is considerably shorter than the usual saturated carbon-carbon bond (1.54Å), it is therefore a hybrid type, and two phenyl groups in *trans*-stilbene must exist almost in the plane in which ethylenic carbon and hydrogen atoms lie. Such configurations are expected in the cases of α-stilbazole (II) and α-pyridostilbene (III).

The spectra of **A** and **B** are typical of the *trans*- and the *cis*-structure (Fig. 3) and make sure of the above determination.

The conclusion is that a known species of α-stilbazole (**A**) is the *trans*-isomer and the other species (**B**) which was separated by the present author is the *cis*-isomer.

The author wishes to thank Professor S. Kimura of Kyoto University for encouragement, Professor T. Matsu'ura of Hiroshima University and Dr. H. Murata of the Osaka Municipal Technical Research Institute for recording infrared spectra, and Mr. M. Yamaguchi of this laboratory for his helpful assistance.

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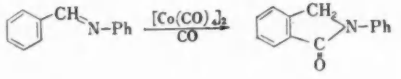
18) R. N. Jones, *J. Am. Chem. Soc.*, **65**, 1818 (1943).
19) J. M. Robertson and I. Woodward, *Proc. Roy. Soc.*, **A162**, 568 (1937).

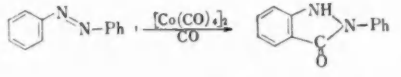
Studies on the High Pressure Reaction of Carbon Monoxide. IV. On the Mechanism of Phthalimidine and Indazolone Formation

By Shigeki HORIIE* and Shunsuke MURAHASHI

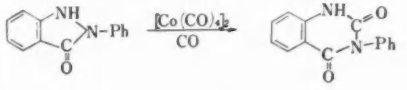
(Received July 3, 1959)

Both the formation of phthalimidines and of indazolones from Schiff bases or azocompounds are considered formally to be the same type of reactions, in which one molecule of carbon monoxide was incorporated into, and then underwent ring closure.





The formation of quinazolons from indazolone is considered to proceed via the reaction of ring enlargement, and has to be considered as another type of reaction and will be mentioned later.



In view of avoiding confusion arising from by-products formation, the reaction of Schiff base was preferably chosen as the subject of this investigation because of the simplicity of the reaction—in the latter case the only reaction product was phthalimidine. From an experiment with Schiff base in continuous run, there could be observed the formation of a complex compound, which was soluble in benzene and was appreciably stable. It was shown in the previous reports that both in the cases of Schiff bases and azobenzenes the more electronegative the "C=N" or "N=N" bond is, the easier the reaction proceeds. These observations seem to indicate that some relation could exist between the ease of complex formation and the feasibility of reaction, and if this argument holds true, the two alternative methods of thinking on the attachment of catalyst on the reactive center of the substrate might be conceivable.

a) The one is that complex formation gives rise to the attachment of cobalt carbonyl across the π-bond of C=N or N=N. In this case a steric requirement

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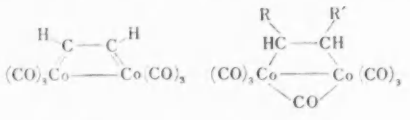
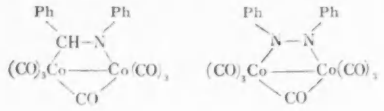
should necessarily be considered as was reported by Wender et al. in the case of oxo-synthesis. They observed the formation of a definite complex[1] from acetylene and cobalt carbonyl of the following constitution and, from this fact they postulated the same kind of complex formation by oxo-reaction, when olefins and cobalt carbonyl were reacted II[2],



(I) (II)

and they reasonably explained the observed differences of reaction velocity on various olefins on the steric ground, which inevitably affects the ease of intermediate complex formation.

If the same arguments are accepted in the authors' case, the intermediate complex would be such as III or IV, and marked steric effect might well be consiedered when Schiff bases or azocompounds were subjected to the experiment.



(III) (IV)

On this account, the authors have compared the velocity of phthalimidine formation reaction, taking benzaldehyde-anil, acetophenone and benzophenone-anil as reactants, and the results are illustrated in Fig. 1. There has been no difference on the velocity and no sterically hindered effect of the phenyl group was discernible. Hence, the formation of this type of complex III would hardly be acceptable.

b) An alternative way of thinking would be that, an attachment of cobalt carbonyl takes place on the lone pair of nitrogen, which gives rise to the formation of a complex, acting as an intermediate for the reaction. Such consideration seems to explain much better the experimental facts which are described below. Although in the case of benzalcyclohexylamine gave in good yield phthalimidine as shown in

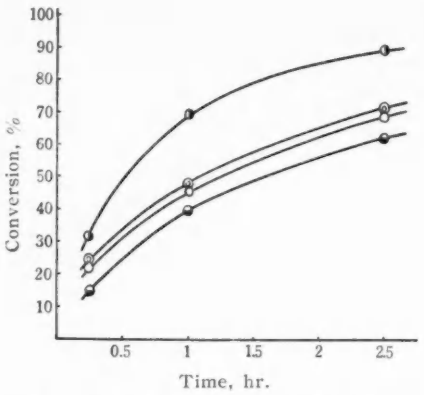
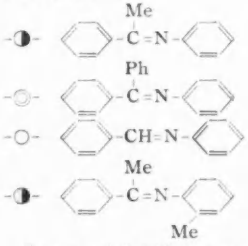
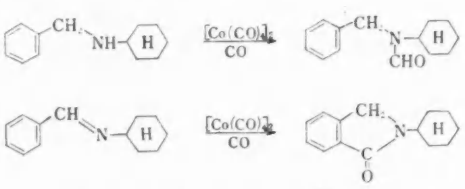


Fig. 1. Reactions of acetophenone-anil and benzophenone-anil with carbon monoxide.



Concn. of Schiff bases: 0.55 millimol/cc.
Concn. of $[Co(CO)_4]_2$: 0.03 millimol/cc.
Pressure of CO : 150 atm.
Solvent : benzene
Reaction temp. : 230°C

formula below, benzyl cyclohexylamine did not give rise to phthalimidine, but only gave *N*-formyl compound by the treatment with carbon monoxide in the presence of cobalt catalyst, under the same condition. Recently, Wender and his collaborators[3] also observed the formation of formyl compounds by the reaction of dimethylamine or piperidine with carbon monoxide, in the presence of cobalt carbonyl catalyst.



In those cases it seems to be appropriate to postulate that an intermediate

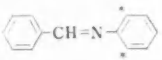
1) H. W. Sternberg, H. Greenfield, R. A. Friedel, J. Wotiz, R. Markby and I. Wender, *J. Am. Chem. Soc.*, **76**, 1457 (1954).

2) I. Wender, S. Metlin, S. Ergun, H. W. Sternberg and H. Greenfield, ibid., **78**, 5401 (1956).

3) H. W. Sternberg, I. Wender, R. A. Friedel and M. Orchin, ibid., **75**, 3148 (1953).

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!NH \xrightarrow[CO]{[Co(CO)_4]_2} \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!N\text{-}CHO$$

formation of a complex occurred resulting from the coordination of the lone pair of the nitrogen atom with cobalt carbonyl, which in turn stabilized to yield formyl compound. Then, as a possible mechanism for the formation of phthalimidine and indazolone, the same argument would be worth while for consideration and for experimentation.



That is, in this case the initial step of the reaction is the coordination of cobalt carbonyl and nitrogen atom of anil bond CH=N, and the steric effect of ortho-position, which are marked with asterisks,

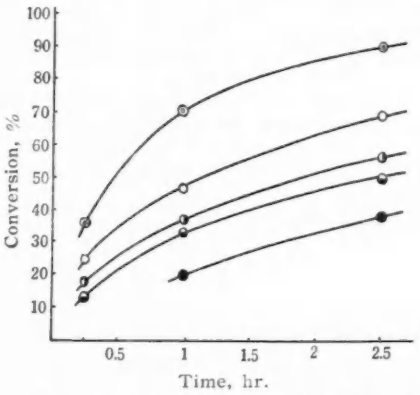
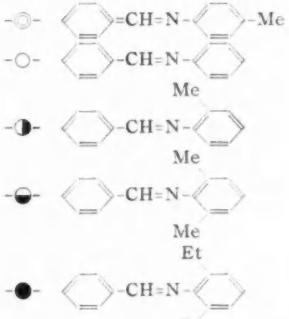


Fig. 2 Reactions of substituted benzaldehyde-anil and carbon monoxide.



Concn. of Schiff bases : 0.55 millimol./cc.
Concn. of $[Co(CO)_4]_2$: 0.03 millimol./cc.
Solvent : benzene
Pressure of CO : 150 atm.
Reaction temp. 230°C

would become very influential to the reaction. Thus, several *o*-substituted anils were subjected to the reaction so as to see whether the steric effect of the substituents was operative. The results of the experiments were illustrated in Fig. 2, where the effect caused by the methyl or ethyl substituent group were visualized in percentage of conversion of anils to phthalimidines, which were followed by the reaction time. It was expected mono-ortho-substituted anil yields lower conversion than unsubstituted one and ortho-dimethyl substituted anil would exhibit a still lesser conversion

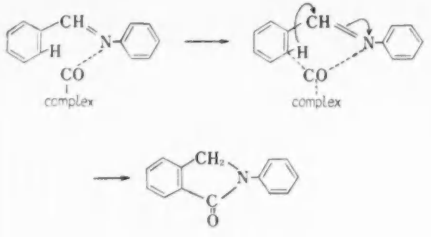
The experiment with *p*-methyl substituted anil has shown that methyl group had rather promoting effect, when it comes on para position, free from steric effect. The fact that in the case of ortho-substituted anil had shown marked low conversion in spite of having a methyl group of promoting action, shows that the steric effect is pronounced in these reactions. Hence it appeared as mentioned above, the primary step would be the addition of cobalt-carbonyl on the lone pair of nitrogen which is hindered by *o*-substituent of large steric requirement.

On the other hand, the reduction of a double bond of anils by means of synthetic gas and cobalt carbonyl go generally smoothly even if in the case where the substituents at the ortho position had shown to exhibit greatest resistance for the formation of phthalimidine, and no distinct steric effect was observed here.

The clear distinction of both reactions should indicate that the fundamental differences might exist in both reactions on the behavior of catalytic action. From the consideration above, the phthalimidine or indazolone formation can eventually be explained as follows.

1) Some kind of complex formation occurred at first between a lone pair of nitrogen atom of the anil or of azo-double bond, and here a steric effect was operative.

2) The formation of N-CO bond was then stabilized with the formation of a 5-membered ring with the carbon atom of benzene with simultaneous transfer of the hydrogen atom of ortho position of benzene to the unsaturated bond of C=N or N=N. Here the presence of such suitable acceptor of hydrogen atom was essential, and these might, side by side, have assisted the ring formation. In the case of benzyl cyclohexylamine as stated above, there is lacking such an accepting group and hence



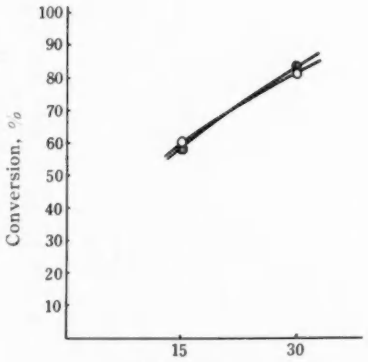
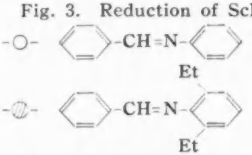


Fig. 3. Reduction of Schiff bases.



Concn. of Schiff bases : 0.5 mmol./cc.
Concn. of $[Co(CO)_4]_2$: 0.03 mmol./cc.
Pressure of synthetic gas : 180 atm.
$CO/H_2=1/1$
Solvent : benzene
Reaction temp. : 120°C

after the formation of the complex would stabilize by converting to formyl benzyl amine.

Concerning the formation of quinazolone from indazolone as the authors stated earlier, it is believed to have formed by a ring-enlargement reaction, and such a reaction, as far as the authors are aware, has not yet been described. A glance at this reaction seems to be similar to the reaction of the formation of diphenylurea from hydrazobenzene, but the mechanism of this enlargement is not yet fully understood.

Experimental

1) Reactions of Schiff Bases and Carbon Monoxide. — *General procedure.* — A solution of 0.0275 mol. of Schiff base and 1.5 millimol. of dicobalt octacarbonyl in 50 ml. benzene was heated at 230°C under 150 atmospheric pressure of carbon monoxide. After the reaction, benzene solution was heated under atmospheric pressure in a water bath so as to decompose cobalt carbonyl and filtered. After removal of benzene by distillation and then under reduced pressure, the residue was analyzed.

On each run, conversions from Schiff base into phthalimidine was determined for every 15, 60 and 150 min.

(i) On benzaldehyde-anil. — Conversions (%) into 2-phenylphthalimidine were 22.9, 46.2 and 68.1, respectively.

(ii) On acetophenone-anil. — Conversions (%) into 2-phenyl-3-methylphthalimidine melted at 82°C were 31.5, 68.5 and 89.0, respectively.

Anal. Found: C, 80.29; H. 5.99. Calcd. for $C_{15}N_{13}ON$: C, 80.69; H, 5.87%.

(iii) On benzophenone-anil.— Conversions (%) into 2,3-diphenyl-phthalimidine melted at 196.5°C were 24.8, 48.6 and 70.2, respectively.

(iv) On acetophenone o-tolylimide.—Conversions (%) into 2-*o*-tolyl-3-methylphthalimidine melted at 108°C were 14.3, 10.0 and 63.5, respectively.

Anal. Found: C, 80.68; H, 6.15. Calcd. for $C_{16}H_{15}ON$: C, 80.98; H, 6.37%.

(v) On benzaldehyde p-tolylimide.—Conversions (%) into 2-*p*-tolylphthalimidine were 36.8, 69.9 and 87.9, respectively.

(vi) On benzaldehyde o-tolylimide.—Conversions (%) into 2-*o*-tolylphthalimidine were 18.2, 36.0 and 53.0, respectively.

(vii) On benzaldehyde o, o-xylidylimide. — Conversions (%) into 2-*o*, *o*-xylidylphthalimidine melted at 103°C were 14.5, 32.8 and 49.8, respectively.

Anal. Found: N, 5.85. Calcd. for $C_{16}H_{15}ON$: N, 5.90%.

(viii) On benzal-o, o-diethylaniline.—Conversions (%) into 2-*o*, *o*-diethylphthalimidine melted at 140°C were 18.6 and 35.9, respectively.

Anal. Found: N, 5.02. Calcd. for $C_{18}H_{19}ON$: 5.28%.

2) Reactions of Benzylcyclohexylamine and Carbon Monoxide.—A solution of 5 g. of benzylcyclohexylamine and 1 g. of dicobalt octacarbonyl in 45 ml. of benzene was heated at 230°C under 140 atmospheric pressure of carbon monoxide to give 1.6 g. (28.1%) of benzylcyclohexylformylamine boiling at 135~140°C/3 mmHg.

Anal. Found: N, 5.99. Calcd. for $C_{14}H_{15}ON$: N, 6.63%.

3) Reaction of Schiff Base and Water Gas.— *General procedure.*—A solution of 0.025 mol. of Schiff base and 1.5 millimol. of dicobalt octacarbonyl in 50 ml. of benzene was heated at 120°C under 180 atmospheric pressure of synthetic gas (CO : H=1 : 1).

A benzene solution obtained was hydrolyzed with 4 N sulfuric acid. Benzaldehyde liberated was determined by the method of Bennett and Salamon[4] (hydroxylamine) to get the amount of unreacted Schiff base.

4) C. T. Bennett and M. S. Salamon; *Analyst*, **52**, 693 (1927).

The percentage conversions of benzal compound to benzyl compound were estimated from the value of Schiff base remaining after 15 and 30 min. in each run.

(i) On benzaldehyde-anil. — Conversions (%) from benzaldehyde-anil into benzylaniline were 59.8 and 80.0, respectively.

(ii) On benzal-o, o-diethylaniline.—Conversions (%) from benzal-*o*, *o*-diethylaniline into benzyl-*o*,*o*-diethylaniline were 58.0 and 81.9, respectively.

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*Radiation-induced Polymerization of α-Methylstyrene**

By Kozo HIROTA, Kenji MAKINO, Keiji KUWATA and Gisuke MESHITSUKA

(Received July 31, 1959)

It has been considered till recently that α-methylstyrene (αMS) is not easily polymerizable, i. e. it can not be polymerized by radical initiators, but can be polymerized by cationic[1] or anionic initiators[2] at low temperatures. Therefore, it will be interesting to study the effect of ionizing radiation on αMS, i. e. to investigate the possibility of radiation-induced polymerization*, and to make clear the kind of mechanism, if it can be polymerized. After the research was advanced to some extent[3], it was found, however, that the first problem was answered affirmatively, and also that the polymerization seemed to proceed by a radical mechanism[3a,b]. Therefore, a new problem was encountered. This was why αMS did not polymerize by use of such a radical initiator as benzoyl peroxide. It is the object of the present paper to investigate the three problems mentioned above.

Experimental

Materials. — α-Methylstyrene of guaranteed grade of Tokyo Kasei Kogyo K. K. was used. It was treated with aqueous solutions of 20% NaOH and of 20% $NaHSO_3$ successively. Then, it was dried with dehydrated calcium chloride and also with potassium hydroxide freshly fused, and vacuum-distilled under nitrogen atmosphere. The sample thus purified was stored in a closed vessel. According to gas chromatographic analysis, the water content in it was negligible (<0.002%). Naphthalene of chemical pure grade was used after repeated recrystallization. Other reagents (carbon tetrachloride, benzoquinone, cyclohexane and nitrobenzene) were of guaranteed grade and were used without further purification.

Procedure of Irradiation.—Two γ-ray irradiation sources of Co-60 were used; one was 350 curie source, while the other 1000 curie source**. Samples will therefore be classified in series B or J, according as the irradiation was carried out at the former or at the latter. In order to avoid direct contact with air and water, αMS was always vacuum-distilled (10^{-4} mmHg) into irradiation tubes. However, as it is known that the presence of oxygen and water brings about an undesirable effect on polymerization, one of the samples (J 9) was distilled over an evaporated film of sodium in advance of irradiation for the sake of comparison. The irradiation tube was made of hard glass and could contain 5~16 g. of αMS. Being required by the discussion on the mechanism of polymerization, ultraviolet irradiation was also attempted by utilizing the sunlight in summer, enclosing the sample in a quartz ampoule.

Treatment of the Irradiated Samples. — The irradiated sample was taken out by opening the tube and was poured into methanol, which was five times as much as the sample in volume. White polymers thus precipitated were filtered, washed with methanol, and dried in vacuo at room temperature until the weight became constant. The molecular weight of the polymer was determined with the osmotic pressure method or the viscosity method. In the latter method,

* When the authors' preliminary research was announced at the 11th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1958, they could not find any research of this kind in literature.

1) D. J. Worsfold and S. Bywater, *J. Am. Chem. Soc.*, **79**, 4917 (1957); S. Okamura et al., Presented at the 7th Annual Meeting of the Society of Highpolymer Science of Japan, Tokyo, May, 1958.

2) G. C. Jones et al., *Ind. Eng. Chem.*, **48**, 2123 (1956).

3) (a) K. Hirota, K. Kuwata and K. Makino, *Isotopes and Radiation* (*Tokyo*), **1**, 104 (1959). (b) Presented at the Symposium of Radiation Chemistry, Tokyo, Nov., 1958.

** The 350 curie source is installed at Institute for Microbial Diseases of Osaka Univ., and the 1000 curie source at Osaka Laboratory of Japanese Association for Radiation Research on Polymers. The authors express sincere thanks to Drs. T. Noguchi, H. Hayashi and M. Hatada for the help in irradiation procedure.

TABLE I. CO-GAMMA IRRADIATION. TOTAL DOSE: 6×10^6 r

	Additives: Compounds	Additives: Mole fraction %	Conversion %	$\bar{M}_n$	m. p. of polymers °C
B-1	None	—	4.4	3.8×10^4	220
B-2	Carbon tetrachloride	18.1	8.2	1.4×10^4	185
B-3	Naphthalene	7.9	0.27	6.0×10^4	195
B-4	Oxygen	air-saturated	0[a]	—	—
B-5	*p*-Benzoquinone[b]	0.41	0	—	—

a) However, when the irradiated sample was poured into methanol, a turbid solution was obtained.

b) Total dose of 7.3×10^6 r; dose rate of 5.3×10^4 r/hr.

the following viscosity formula was used[4].

$$[\eta] = 3.50\times10^{-5}(\bar{M}_n) \quad (1)$$

$\bar{M}_n$: average molecular weight

As the molecular weight of the polymer was low in case of photopolymerization, the cryoscopic method was adopted.

Results

Preliminary Experiments. — As shown in Table I, it has been found that αMS polymerizes with total dose of 6×10^6 r, dose rate being 1.2×10^5 r/hr. The polymer obtained is of fairly high molecular weight. Its melting point is also high if compared with the polymer obtained by photo-polymerization[5]. Moreover, it has been found that polymerization was sensitized by the addition of carbon tetrachloride, but was retarded by the presence of naphthalene and perfectly inhibited by oxygen and benzophenone. Such effects of additives seem to suggest that the polymerization proceeds by the radical initiation of γ-rays.

Effect of Total Dose. — In Table II, the effect of total dose on conversion and intrinsic viscosity is shown by keeping the dose rate constant. Conversion of polymerization increases linearly with the total dose after an induction period (ca. 5 hr.). On the other hand, judging from the relation between the intrinsic viscosity and total dose, the molecular weight of the polymer seems to be constant.

TABLE II. EFFECTS OF TOTAL DOSE ON CONVERSION AND INTRINSIC VISCOSITY

Run	Dose rate r/hr.	Dose r	Conversion, %	$[\eta]$
J 6-1	1.56×10^5	5.8×10^6	28.2	0.110
J 6-2	1.56×10^5	4.34×10^6	21.4	0.116
J 6-3	1.56×10^5	1.74×10^6	4.4	0.113

4) C. P. Brown and A. R. Mathieson, *J. Chem. Soc.*, 1958, 3445.

5) C. E. Schildknecht, *Ind. Eng. Chem.*, **50**, 107 (1958).

Effect of Dose Rate. — In Table III, the effect of dose rate on conversion is shown. In order to investigate the effect of dose rate on velocity of polymerization in detail, the conversion rate V_p is plotted against dose rate I in Fig. 1. It is clear that the velocity of polymerization of αMS is first order of I on the assumption that it is proportional to the rate of conversion. For the sake of comparison, the result of

TABLE III. EFFECT OF DOSE RATE ON CONVERSION

Run	Dose rate r/hr.	Dose r	Conversion, %	$[\eta]$
J 1-2	2.6×10^4	3.5×10^6	8.6	0.105
J 1-3	1.4×10^4	1.8×10^6	4.6	0.106
J 1-4	8.8×10^3	1.2×10^6	7.5	0.115
J 7-3	1.6×10^5	3.3×10^6	20.5	0.118
J 7-4	1.6×10^5	7.6×10^6	19.1	0.116

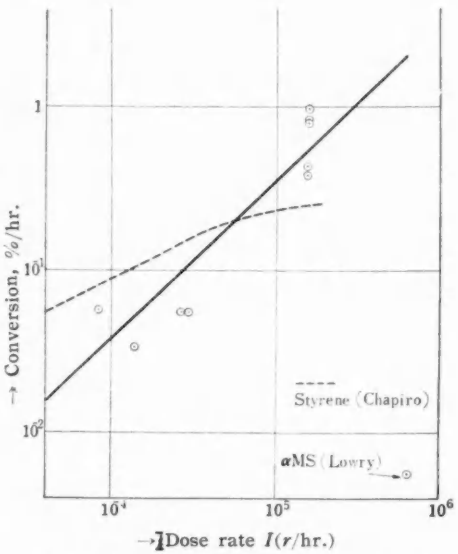

Fig. 1. Conversion per hour vs. dose rate.

Chapiro[6] on styrene is plotted as a broken line, by which it is shown that the order of polymerization of styrene is one half if the dose rate is small. The same order is often reported in the γ-ray-induced polymerization. Therefore, it may be noteworthy that an exceptional order of reaction has been obtained in the present research. This problem will be taken up again in the part of discussion in relation to the mechanism of polymerization. However, the polymerization velocity seems of the same degree in both monomers, while the recent data of Lowry[7] on αMS is very small as compared with that of the present research. The intrinsic viscosity $[\eta]$ is shown to be independent of dose, i. e. 0.110, being similar to that of Lowry. The molecular weight of poly-α-methylstyrene is smaller than that of polystyrene by Chapiro.

Effect of Solvent. — As mentioned in the part of the preliminary experiment, effect of several solvents on the reaction rate was already investigated. However, an additional experiment was carried out in other solvents, in order to make the mechanism of polymerization clearer. To meet this requirement, nitrobenzene and cyclohexane were selected as the solvents to be studied, each dielectric constant being 36 and 1.9, respectively. If the reaction proceeds by an anionic or cationic mechanism, αMS will polymerize very rapidly in a solvent of high dielectric constant[8] such as nitrobenzene, while if the reaction proceeds by a radical mechanism, the polymerization must be inhibited by the solvent on the contrary. According to the result shown in Table IV, nitrobenzene behaves as an inhibitor, while cyclohexane behaves as a simple diluent. The result, in addition to the preliminary experiments, confirms the conclusion that the reaction proceeds by a radical mechanism.

Effect of Temperatures.—Hitherto, radical polymerization of αMS has been attempted at higher temperatures, but the result was found always negative. Though the data here obtained seem to contradict the above results, the situation may be brought about by the condition that the irradiation was carried out at ordinary temperature. Such being the case, the effect of temperature on radiation-induced polymerization was investigated over the range 9~72°C, the result being summarized in Table V.

As shown by the value of intrinsic

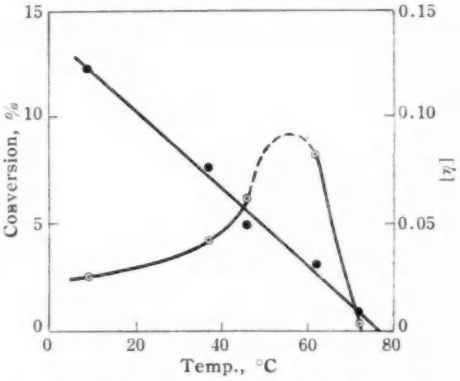

Fig. 2. Conversion and intrinsic viscosity vs. temperature.
⊙: Conversion, %
●: Intrinsic viscosity, $[\eta]$

TABLE IV. EFFECT OF SOLVENT ON THE RATE OF POLYMERIZATION

Run	Additive compounds	Mol. %	Dose rate r/hr.	Dose r	Conversion %	$[\eta]$
J 7-1	Cyclohexane	29.0	1.6×10^5	3.4×10^6	13.2	0.101
J 7-2	Nitrobenzene	37.3	1.6 〃	3.4 〃	0	—

TABLE V. EFFECT OF TEMPERATURE ON CONVERSION etc.

Run	Temp. °C	Dose rate r/hr.	Dose r	Conversion %	$[\eta]$	$\overline{DP}$
J 9-1	9	3.1×10^4	1.2×10^6	2.5	0.123	29.6
J 9-2	37	〃	〃	4.2	0.076	18.6
J 9-3	46	〃	〃	6.1	0.049	11.9
J 9-4	62	〃	〃	8.2	0.030	7.3
J 9-5	72	〃	〃	0.33	0.009	2.2

6) A. Chapiro and P. Wahl, *Compt. rend.*, **238**, 1803 (1954).
7) G. G. Lowry, *J. Polymer Sci.*, **31**, 187 (1958).
8) D. C. Pepper, *Trans. Faraday Soc.*, **45**, 397 (1949).

viscosity, it seems that the degree of polymerization $\overline{DP}$ decreases linearly with temperature, and will became practically zero at 77°C. This tendency may be clearly shown by Fig. 2 where conversion and $[\eta]$ are plotted against temperature. It may be estimated that the degree of polymerization at 77°C will be less than five, because telomers of such low polymerization degree are soluble in methanol. On the other hand, the amount of conversion has a maximum and will be zero at 72°C (cf. Fig. 2). The phenomenon here observed must be ascribed to the peculiar property of αMS, and will serve as a key to the mechanism of polymerization***.

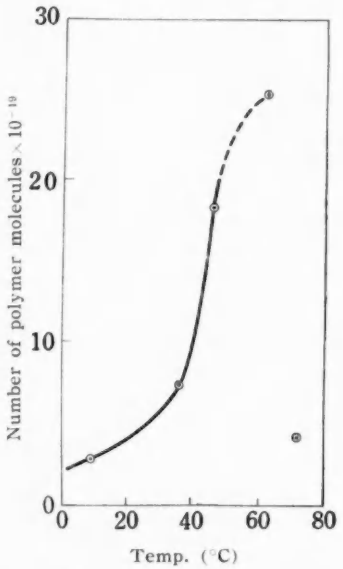

Fig. 3. The effect of temperature on the number of polymer molecules.

Assuming that Eq. 1 can be applied on the poly-αMS, as far as the relative value of average molecular weight is concerned, the number of polymer (n) produced at each temperature was calculated, and it was found that n increases very rapidly if temperature decreases as shown in Fig. 3.

Photopolymerizations. — Recently, it was reported that Schildknecht[5] succeeded to polymerize αMS by irradiating it with ultraviolet light, the detail being not described. Therefore, similar research was carried out by use of the sunlight for the sake of confirmation. Polymers of 0.38 g. in weight could be obtained from the starting material of (αMS 15.7 g.+di-*tert*-BPO 4.0 g.). The molecular weight of the polymers was ca. 640 (cryoscopic method).

*** Detailed discussion on the relations of conversion and intrinsic viscosity with temperature will be omitted, because it was published already [K. Makino, G. Meshitsuka, K. Kuwata and K. Hirota, *Isotopes and Radiation (Tokyo)*, **2**, 322 (1959)].

Discussion

Mechanism of Polymerization.—Considering the effects of additives and solvents on the yield of polymers, it may be reasonable to conclude that the radiation-induced polymerization of αMS proceeds by a radical mechanism, as already mentioned. Polymerizing power of ultraviolet light also supports the mechanism, though telomers obtained are of low molecular weight. In the course of the present research this conclusion has been justified independently by Lowry[7] who could obtain polymers having the molecular weight of 50000 at 0°C by the redox polymerization method.

Thus, the present research seems merely to have added an example of radiation-induced polymerization, but it may be noteworthy to have found that the polymerization of this monomer has a peculiar dependency upon temperature, especially it will practically stop at higher temperatures than ca. 70°C. Now, it may be clear why the attempts to polymerize αMS did not succeed hitherto. In these attempts the temperatures to supply radical initiators to the sample were too high to obtain polymers. The phenomenon of this kind called "ceiling temperature" was already pointed out experimentally by Snow and Frey[9] in the copolymerization of olefins and sulfur dioxide. Later Dainton and Ivin[10] explained it by assuming the equilibrium

$$M_j + M \rightleftarrows M_{j+1}$$

and derived the existence of a temperature beyond which the reaction chains will fail to grow. Thermodynamically the ceiling temperature T_c may generally be given by

$$T_c = -\Delta H_p / -\Delta S_p = \frac{\Delta H}{\Delta S^\circ + 2.30 R \log_{10}[M]} \quad (2)$$

where ΔH_p and ΔS_p denote, respectively, changes of enthalpy and entropy of polymerization, [M] denotes the concentration

9) R. P. Snow and F. E. Frey, *Ind. Eng. Chem.*, **30**, 176 (1938); *J. Am. Chem. Soc.*, **65**, 2417 (1943); cf. F. E. Mathews and H. M. Elder, Brit. Pat., 11,635 (1914).
10) F. S. Dainton and K. Ivin, *Nature*, **162**, 705 (1948).

of monomer, and S° denotes the quantity referred to monomer in a standard state of pure liquid. Recently McCormic[11] determined T_c of αMS to be 61°C from the polymerization in tetrahydrofuran solution by use of a sodium naphthalene complex as initiator. Though the temperature is slightly lower than that of the present research, the discrepancy can be explained by Eq. 2, if it is considered that the degree of polymerization of the present sample is lower than that of McCormic (cf. the formula[12] giving the relation between ΔH_p and average molecular weight $\overline{M}_n$: $-\Delta H_p = 8.424 + 2194/\overline{M}_n$). It is rather interesting that T_c of such a low temperature is obtained in both experiments, notwithstanding the fact that the active species are different in the course of polymerization. Now, a problem remains why T_c of poly-α-methylstyrene is much lower than that of polystyrene. It may be ascribed to the small values of $-\Delta H_p$ for this monomer as compared with other monomers: e. g. αMS 9.0, styrene 16.0 and ethylene 22, respectively in kcal./mol. per monomer, in spite of the order of magnitude of its ΔS_p comparable to the other monomers[13].

Kinetic Formula of Polymerization. — From the above discussion, it seems to be without ambiguity that radiation-induced polymerization of αMS proceeds by a radical mechanism, but an important experimental result still remains to be unexplained. In the pioneer work of Chapiro[6] on the gamma-ray-induced polymerization of styrene and other monomers, he found that velocity V_p of the polymerization can be expressed by the formula

$$V_p \propto I^{1/2} \tag{3}$$

where I is the dose rate. The formula is generally accepted to be applicable to all the radiation-induced polymerization. Nevertheless, in the present research as shown in Fig. 1, the velocity derived from the conversion (%) is not proportional to $I^{1/2}$ but rather to I. The above result, though it seems to be exceptional, can be understood by the mechanism in which a degradative chain transfer proceeds more frequently than the chain termination between radicals. Therefore, each step of the elementary processes of the present reaction will be summarized as follows:

Initiation: $\mathrm{M} \xrightarrow{\phi I} \mathrm{R}\cdot$

$\mathrm{R}\cdot + \mathrm{M} \xrightarrow{k'_i} \mathrm{M}^*$

Propagation: $\mathrm{M}^*_j + \mathrm{M} \xrightarrow{k_p} \mathrm{M}^*_{j+1}$

Depropagation: $\mathrm{M}^*_{j+1} \xrightarrow{k_d} \mathrm{M}^*_j + \mathrm{M}$

Chain transfer to monomer:

$\mathrm{M}^*_j + \mathrm{M} \xrightarrow{k_{tr}} \mathrm{M}_j + \mathrm{M}^*$

Degradative chain transfer:

$\mathrm{M}^*_j + \mathrm{M} \xrightarrow{k_t} \mathrm{M}_j + \mathrm{M}$

where M^*_j denotes active polymers of j subunits and ϕ radicals produced per unit I in unit volume of monomers. Applying the steady state treatment to the mechanism mentioned above, the kinetic formula may be derived easily:

$$V_p = (\phi I/k_t)(k_p[\mathrm{M}] - k_d)$$

i. e. V_p is proportional to I.

Summary

It has been shown that (a) α-methylstyrene polymerizes at room temperatures by gamma-ray irradiation; that (b) the reaction proceeds by a radical mechanism, considering from the effect of solvents, additives and ultraviolet light; that (c) ceiling temperature for this monomer is exceptionally low (ca. 70°C) among vinyl monomers, so that it is hard to obtain high polymers by the usual method; that (d) the experimental fact that the velocity of polymerization is proportional to dose rate and not to square root of dose rate can be explained by the assumption that degradative chain transfer occurs more frequently than the termination between active polymers.

A part of the expense for the present experiment has been defrayed from a grant given by the Ministry of Education, to which the authors' thanks are due.

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11) H. W. McCormick, *J. Polymer Sci.*, **25**, 488 (1957).
12) D. E. Roberts and R. S. Jessup, *J. Res. Natl. Bur. Standards*, **38**, 627 (1947).
13) C. Walling, "Free Radicals in Solutions", John Wiley & Sons, Inc., New York (1957), p. 213; F. S. Dainton and K. J. Ivin, *Quart. Revs.*, **12**, 61 (1958).

Solvent Effect on the Intrinsic Viscosity of Polymers

By Tetsuya ISHIKAWA

(Received July 7, 1959)

It is well known that the intrinsic viscosity, $[\eta]$, of a polymer takes high values in good solvents and low values in poor solvents. If the experimental precautions to be observed in order to obtain reliable data are taken, such difference may be attributed quantitatively to the solvent character which the existing theories of dilute solution viscosity of polymers do not deal with.

Analytical Procedure

In the last report[1], the author derived from his ideal mixture law for viscosity the following form for $[\eta]$, $cm^3\,g^{-1}$:

$$[\eta] = \frac{(K_v)_0}{d_2}\left(\frac{\eta_2}{\eta_1}\right),$$

$$(K_v)_0 = \left.\frac{(1-z_v)(\eta-\eta_1)}{z_v(\eta_2-\eta)}\right]_{z_v\to 0} \qquad (1)$$

in which η_1, η_2 and η denote the viscosities of a solvent, solute of high molecular weight whose density is d_2, and the solution respectively, and z_v is the volume fraction of the solute before mixing.

For an ideal mixture composed of two liquids of low molecular weights, $(K_v)_0 = (K_v)_1 = K_v$, a constant for all concentrations, and the probable values of K_v relative to benzene of 32 liquids can be computed from K values relative to benzene obtained before[2], by means of the equality:

$$K_v = K\frac{M_1 d_2}{M_2 d_1} \qquad (2)$$

where M_1, M_2, and d_1, d_2 are the molecular weights and densities of components 1 and 2, respectively, benzene being taken as component 1 in this case.

Combining Eq. 1 with Eq. 2, the following assumption is made:

Since $[\eta]$ is an extrapolated value at infinite dilution of a polymer with a given solvent where solvent molecules suffer presumably no change in association, $(K_v)_0$ of polymer/solvent may be inversely proportional to K_v of solvent/benzene, and therefore $[\eta]$ may be inversely proportional to the product

$$\eta_1 \times (K_v \text{ of solvent/benzene})$$

so long as $(K_v)_0 \times (K_v$ of solvent/benzene) which signifies the solute character term at infinite dilution retains a constant value in different solvents.

In other words, between the intrinsic viscosities of the same polymer in solvent 1 and in solvent 2, there may exist the equation:

$$\frac{[\eta] \text{ in solvent 1}}{[\eta] \text{ in solvent 2}} = \frac{(\eta \times K_v \text{ rel. to benzene}) \text{ of solvent 2}}{(\eta \times K_v \text{ rel. to benzene}) \text{ of solvent 1}} \qquad (3)$$

Verifications

In order to verify Eq. 3, one quotes from Wales, Marshall and Weissberg's report on the intrinsic viscosities of dextran in water and in formamide at 25°C[3], as one has $K=0.67$ for water and $K=0.34$ for formamide at 25~40°C[2].

Now, one has for benzene ($M=78.11$) $d=0.87875$(20/4), 0.86805(30/4); for water ($M=18.02$) $d=0.99823$ (20/4), 0.99568 (30/4), $\eta=0.01005$ poise (20°C), 0.00802 poise (30°C); and for formamide ($M=45.04$) $d=1.1349$ (20/4), 1.1266(30/4), $\eta=0.0375$ poise (20°C), 0.0294 poise (30°C)[4,5].

From these values one obtains

$$\frac{(\eta \times K_v \text{ rel. to benzene}) \text{ of water}}{(\eta \times K_v \text{ rel. to benzene}) \text{ of formamide}} = 1.16(20°C),\ 1.19(30°C)$$

On the other hand, the inverse ratios of intrinsic viscosity values, $100\,cm^3\,g^{-1}$, in formamide to those in water taken from

1) T. Ishikawa, This Bulletin, **31**, 791 (1958).
2) T. Ishikawa and T. Baba, ibid., **11**, 64 (1936); see also T. Ishikawa, ibid., **31**, 524 (1958).
3) M. Wales, P. A. Marshall and S. G. Weissberg, *J. Polymer Sci.*, **10**, 229 (1953).
4) "International Critical Tables", III, (1928), pp. 25, 27—30.
5) F. Henning, "Wärmetechnische Richtwerte", Vdi-Verlag G.m.b.H. (1938), pp. 40—45.

Wales, Marshall and Weissberg's data for dextran of four different molecular weights, M, are:

$$\frac{[\eta] \text{ in formamide}}{[\eta] \text{ in water}} = \frac{0.121}{0.097} = 1.25 \text{ for } M = 11000$$

$$= \frac{0.341}{0.271} = 1.26 \text{ for } M = 71000$$

$$= \frac{0.446}{0.384} = 1.16 \text{ for } M = 153000$$

$$= \frac{0.492}{0.421} = 1.17 \text{ for } M = 185000$$

Comparing these values with the above obtained values, it is seen that the coincidence is satisfactory, especially for dextran of higher molecular weights.

The following is another test applied to the data of the toluene and methyl ethyl ketone (MEK) solutions of one polystyrene sample distributed to several laboratories from the International Union of Pure and Applied Chemistry (IUPAC)[6]. The average values of $[\eta]$, cm^3g^{-1}, assembled by Frank and Mark were 148.3±2.3 for toluene at an average temperature 25.5°C (25°C in eight laboratories, 30°C in one laboratory, and 24.7°C in one laboratory), and 82.9±2.8 for MEK at an average temperature 25.5°C (25°C in seven laboratories, 30°C in one laboratory, and 24.7°C in one laboratory).

For toluene one has $\eta = 0.00551$ poise (25°C)[7], and $K = 1.24$ (15~35°C)[2], from which one gets $K_v = 1.03$ (25°C) by putting toluene ($M = 92.13$) and benzene ($M = 78.11$) densities to be 0.86122 (25/4) and 0.87340 (25/4), respectively; for MEK one has $\eta = 0.00383$ poise (25°C) but K is unknown because of lack of binary mixtures composed of this liquid as one component in the literature, and, under the author's direction, viscosity measurements on the binary system of benzene (1)-MEK(2) have been carried out by M. Ikeda, lecturer of Nagasaki Prefectural Junior College.

Benzene and MEK used for the present measurements were the guaranteed reagents of Kanto Chemical Co., Inc., the former having test No. 4E033294 and the latter having test No. 3E088722, and both were used without further purification.

Densities and viscosities were measured at 25°C with an automatically regulated thermostat, T-3 type of Shimadzu Seisakusho Ltd., with a Gay-Lussac pycnometer of 25 cm^3, and with a Ostwald viscometer with 10 cm^3 efflux volume which has given efflux time of 54.70 sec. for water.

To convert density (25/25) to density (25/4) and relative viscosity to absolute viscosity, the author used density of water at 25°C = 0.99707[4], and viscosity of water at 25°C = 0.008941 poise[8].

TABLE I. BENZENE(1)—METHYL ETHYL KETONE(2), 25°C

z_v	d_4^{25}	η_{obs}	K_v obs.	K_v cacld.	η_{calcd}
0.000	0.8733	0.006158		(1.79)	—
0.125	0.8646	0.005655	2.16	1.86	0.005710
0.250	0.8557	0.005323	1.93	1.94	0.005320
0.375	0.8467	0.004977	2.07	2.03	0.004982
0.500	0.8377	0.004727	2.04	2.13	0.004713
0.625	0.8286	0.004511	2.02	2.23	0.004477
0.750	0.8191	0.004296	2.28	2.35	0.004294
0.875	0.8096	0.004137	2.55	2.48	0.004145
1.000	0.7999	0.004024		(2.63)	—

The experimental results are given in Table I. As seen from the observed K_v values in Table I, this system belongs to the case where the association degree of either of the components decreases with the dilution of the other, and either of the extrapolated values of K_v at $z_v = 0$ or $z_v = 1$ gives the normal K_v for the mixture. Mixtures of phenol, guaiacol, or benzyl benzoate with benzene or toluene in which the former components suffer molecular dissociation are examples for this case. The formulation of viscosity vs. composition curves of such mixtures can not be generally done, yet a particular case can be solved by a particular means, that is to say, K_v or its reciprocal at each composition to test whether they are in linear relationship with composition or not[9]. For the present case, reciprocal values of K_v against z_v appear to lie nearly on a straight line, $1/K_v = 0.56 - 0.18\,z_v$, hence one has obtained $(K_v)_0 = 1.79$ and $(K_v)_1 = 2.63$. Compare the observed and calculated viscosity values in Table I, the deviations being at most less than 1%. It is doubtful, however, that either of components, benzene or MEK, suffers molecular dissociation, so the author refers to the results by making use of Fischler's viscosity data on benzene

6) IUPAC, *J. Polymer Sci.*, **17**, 1 (1938).
7) T. E. Thorpe and J. W. Rodger, *Phil. Trans. Roy. Soc. London. Ser.* **A185**, 397 (1894); J. Batschinski, *Z. physik. Chem.*, **84**, 643 (1913).
8) "Landolt-Börnstein Tabellen", Eg. I, p. 83.
9) T. Ishikawa, This Bulletin, **4**, 288 (1929); refer also to 2).

(1)-acetone(2) system[10] as found in the literature (see Table II). Since in this system benzene suffers no molecular change throughout the concentration, giving a constant value 2.06 ± 0.05 which is an intermediate value between $(K_v)_0$ and $(K_v)_1$ for MEK/benzene, the same liquid in the benzene(1)-MEK(2) system may also be considered to suffer no molecular change, and therefore $(K_v)_1=2.63$ can be decided as the normal value, K_v, for MEK/benzene, the corresponding association degree of MEK being estimated to be 2.78.

TABLE II. BENZENE(1)—ACETONE(2), 25°C (FISCHLER)

z_v	η	K_v
0.00	0.005758	
0.25	0.004715	2.00
0.50	0.003997	2.08
0.75	0.003507	2.10
1.00	0.003150	
		2.06 ± 0.05

Taking $K_v=2.63$ and $\eta=0.00383$ poise at 25°C for MEK and the above values for toluene, one obtains

$$\frac{(\eta\times K_v \text{ rel. to benzene) of MEK}}{(\eta\times K_v \text{ rel. to benzene) of toluene}}=1.77$$

whereas

$$\frac{[\eta] \text{ in toluene}}{[\eta] \text{ in MEK}}=\frac{148.3}{82.9}=1.79$$

for $M=560000\sim590000$

Also from the similar data on four polystyrene fractions in the previous report[11] from IUPAC, the same ratios in respective laboratories are:

$$\frac{[\eta] \text{ in toluene}}{[\eta] \text{ in MEK}}=1.88,\ 1.99 \text{ for } M=860000$$
$$=2.11,\ 2.01 \text{ for } M=655000$$
$$=1.54,\ 1.61 \text{ for } M=234000$$
$$=1.64,\ 1.60 \text{ for } M=82500$$

with an average of 1.80 which is nearly equal to the preceding result. Hence the coincidence is fairly good between the ratios taken from intrinsic viscosity data and from the present theory.

Conclusion

The foregoing verifications lead us to the conclusion that an intrinsic viscosity equation $[\eta]=(K_v)_0(\eta_2/\eta_1)/d_2$ is valid for polymer solutions, and therfore that $[\eta]$ of a polymer in a solvent can be converted to $[\eta]$ of the same polymer in a standard solvent, e. g. benzene, or toluene, or acetone; this procedure will give a reliable value to be further analyzed, if normal K_v values of these solvents relative to the standard solvent are known.

The author is indebted to Nagasaki American Cultural Center for having made it possible for him to obtain, by mail from Tokyo, Journal of Polymer Science, Vol. X, 1953; and also to Mr. M. Ikeda for his viscosity measurements on the binary system of benzene and methyl ethyl ketone.

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10) J. Fischler, *Z. Elektrochem.*, **19**, 126 (1913).
11) IUPAC, *J. Polymer Sci.*, **10**, 129 (1953).

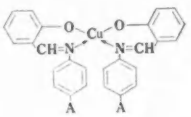
Some Addition Compounds of Salicylaldehyde-ethylenediimine-copper. IV.*

By Tsuguo TANAKA

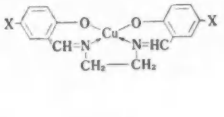
(Received August 17, 1959)

Recently, some observation have been reported[1] about the influence of substituents in the ligand molecules on the physical and chemical properties of their metal chelates. Calvin et al.[2] presented the following order about the stability of the chelates, which he explained on the basis of mesomeric effect, among the substituents A in a metal chelate of salicylaldehyde-anil (I) by the measurement of their half wave potential.

$$OCH_3 > OH > CH_3 > H > C_6H_5 > SO_3Na > NO_2$$



(I)



(II)

An analogous but not identical order of substituents was also observed by the present author[3] about the tendency of the formation of the addition compounds of 5,5′-disubstituted salicylaldehyde-ethylenediimine-copper (II) with propionic acid, phenol and chloroform; the order was

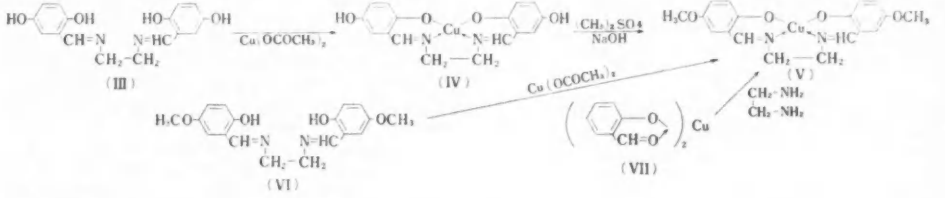
$$5,5'\text{-}CH_3 > 5,5'\text{-}H > 5,5'\text{-}NO_2 > 5,5'\text{-}Cl$$

Now, it was attempted to obtain a further illustration about the influence of the 5,5′-substituent groups in salicylaldehyde-ethylenediimine-copper on the formation of the addition compounds.

5,5′-Dibromo-, 5,5′-diiodo- and 5,5′-dimethoxy-salicylaldehyde-ethylenediimine-copper were synthesized according to the usual procedure[3,4]. 5,5′-Dibromosalicylaldehyde-ethylenediimine-copper was obtained as a purple addition compound with chloroform when it was recrystallized from chloroform, which was eliminated on standing in the air to give a pure green 5,5′-dibromo-salicylaldehyde-ethylenediimine-copper.

The metal chelate which was obtained by the reaction of 5-iodosalicylaldehyde-copper with ethylenediamine-monohydrate in an ethanolic solution was a purple addition compound of 5,5′-diiodosalicylaldehyde-ethylenediimine-copper with ethanol which lost ethanol, when heated at 110°C for thirty minutes, to give dark green 5,5′-diiodosalicylaldehyde-ethylenediimine-copper. Free 5,5′-diiodosalicylaldehyde-ethylenediimine-copper formed addition compounds with ethanol and chloroform.

But the reaction of 5-hydroxysalicylaldehyde with copper acetate in an ethanolic solution resulted in the formation of a black polymeric copper salt, which could not be converted into 5,5′-dihydroxysalicylaldehyde-ethylenediimine-copper by a reaction with ethylenediamine in ethanol. Therefore, 5-hydroxysalicylaldehyde was treated with ethylenediamine-monohydrate in an ethanol to give 5,5′-dihydroxysalicylaldehyde-ethylenediimine (III), which on warming in ethanol with an aqueous solution of copper acetate produced dark blue crystals of the copper salt (IV)[5]. The structure of 5,5′-dihydroxysalicylaldehyde-ethylenediimine-copper (IV) was



(III) (IV) (V) (VI) (VII)

* Bis-salicylaldehyde-ethylenediimine-copper.

1) M. Calvin and K. W. Wilson, *J. Am. Chem. Soc.*, **67**, 2003 (1945). L. G. G. van Uitert, W. C. Fernelius and B. E. Douglas, ibid., **75**, 457 (1953).

2) M. Calvin and R. H. Bailes, ibid., **68**, 953 (1946).

3) T. Tanaka, ibid., **80**, 4108 (1958).

4) P. Pfeiffer, E. Breith, E. Lübbe and T. Tsumaki, *Ann.*, **503**, 85 (1933).

5) C. S. Marvel and N. Tarkoy, *J. Am. Chem. Soc.*, **80**, 832 (1958).

TABLE I. ADDITION COMPOUNDS OF SALICYLALDEHYDE-ETHYLENEDIIMINE-COPPER DERIVATIVES

Substituents	Color of complex	Addition compounds Color (time required for formation, min.)			
		Propionic acid	Phenol	Chloroform	Ethanol
5,5'-OCH_3[a]	yellow green	purple brown (2)	purple (0.5)	—	—
5,5'-I	dark green	purple (6)	purple (0.5)	purple (0.5)	purple[b]
5,5'-OH[a]	gray green	—	purple brown (0.5)	—	—
5,5'-Br	green	—	purple (0.5)	purple[b]	—

a) Powdered sample. b) Recrystallization.

confirmed by the following synthesis.

5,5'-Dihydroxysalicylaldehyde-ethylenediimine-copper (IV) was methylated by treating it with dimethylsulfate and aqueous sodium hydroxide[6], when 5,5'-dimethoxysalicylaldehyde-ethylenediimine-copper (V) was obtained. V was also obtained either by the reaction of 5,5'-dimethoxysalicylaldehyde-ethylenediimine (VI) with an aqueous solution of copper acetate in ethanolic solution, or by the reaction of 5-methoxysalicylaldehyde-copper (VII) with ethylenediamine-monohydrate. Identity of these products was proved by the observation of the absorption spectra.

The formation of the addition compounds of these metal chelates with propionic acid, phenol, chloroform and ethanol was examined and the results were summarized in Table I.

Peculiar behavior of 5,5'-diiodosalicylaldehyde-ethylenediimine-copper was noted; it formed addition compounds with propionic acid as well as with chloroform and ethanol in contrast to other derivatives.

Comparing these results with those already reported, the tendency of the formation of addition compounds is in the following order,

$$\underset{(+)}{5,5'\text{-}CH_3} > \underset{(-)}{5,5'\text{-}OCH_3} > \underset{(-)}{5,5'\text{-}I} > 5,5'\text{-}H >$$
$$\underset{(-)}{5,5'\text{-}OH} > \underset{(-)}{5,5'\text{-}Br} > \underset{(-)}{5,5'\text{-}NO_2} > \underset{(-)}{5,5'\text{-}Cl}$$

where (+) indicates electron releasing and (−) electron attracting inductive effects[7].

Experimental

5-Iodosalicylaldehyde was obtained as its sodium salt by the reaction of *p*-iodophenol (10 g.) with chloroform (9 g.) in aqueous sodium hydroxide[8] (9.1 g. sodium hydroxide in 40 ml. water) at 55~65°C. Yield, 14%.

5, 5'-Dihydroxysalicylaldehyde - ethylenediimine. —To a solution of 5-methoxysalicylaldehyde (1.6 g. in 41 ml. ethanol) was added ethylenediamine-monohydrate (520 mg. in 5 ml. ethanol). In the meantime a yellow precipitate separated, which was filtered and dried (1.5 g.). It was dissolved in ethanol and water was added to it drop by drop until turbidity occurred; the product was left to stand for a while, until yellow needles separated, which were filtered and dried. Yield, 0.9 g.; m. p. 250°C (decomp.). It is easily air-oxidized in an ethanolic solution, when left to stand for one day and the color changes into orange to red.

Anal. Found: C, 60.63; H, 5.77; N, 8.00. Calcd. for $C_{16}H_{16}O_4N_2$-H_2O: C, 60.37; H, 5.70; N, 8.80%.

5,5'-Dimethoxysalicylaldehyde - ethylenediimine. —To a solution of 5-methoxysalicylaldehyde (900 mg. in 20 ml. ethanol) was added ethylenediamine-monohydrate (100 mg. in 3 ml. ethanol). In the meantime the whole mass solidified, which was filtered, washed with a little water and recrystallized from ethanol. Yield, 700 mg.; m. p. 165°C.

Anal. Found: C, 65.95; H, 6.38; N, 8.29. Calcd. for $C_{18}H_{20}O_4N_2$: C, 65.84; H, 6.14; N, 8.53%.

5,5'-Dibromo-, 5,5'-diiodo-, 5,5'-dimethoxysalicylaldehyde-ethylenediimine-copper were obtained by the usual procedure[3,4].

5, 5' - Dibromosalicylaldehyde - ethylenediimine - copper. —Gold orange 5-bromosalicylaldehyde-copper was converted into green 5,5'-dibromosalicylaldehyde-ethylenediimine-copper. Recrystallization of the product from chloroform produced a purple addition compound with chloroform which, upon standing in air, gradually (in two days) lost chloroform to yield the green, pure 5,5'-dibromo-complex.

Anal. Found: C, 39.99; H, 2.86; N, 5.91; Cu, 13.04. Calcd. for $C_{16}H_{12}O_2N_2Br_2Cu$: C, 39.42; H, 2.48; N, 5.75; Cu, 12.97%.

5, 5' - Diiodosalicylaldehyde - ethylenediimine - copper.—Gold yellow 5-iodosalicylaldehyde-copper suspended in boiling ethanol was treated with ethylenediamine-monohydrate; immediately transient green coloration was observed, but the color turned purple and the purple addition compound of 5,5' - diiodosalicylaldehyde - ethylenediimine-copper with ethanol precipitated, which was filtered and recrystallized from ethanol. By heating the addition compound at 110°C for thirty minutes, dark green pure 5,5'-diiodosalicylaldehyde-ethylenediimine-copper was obtained.

6) H. Decker and O. Koch, *Ber.*, **40**, 4794 (1907).
7) C. K. Ingold, *Ann. Repts.*, **23**, 129 (1926).
8) Cf. also H. H. Hodgson and T. A. Jenkinson, *J. Chem. Soc.*, **1927**, 1740; ibid., **1929**, 469.

Anal. Found: C, 33.25; H, 2.42; N, 4.17; Cu, 10.40. Calcd. for $C_{16}H_{12}O_2N_2I_2Cu$: C, 33.04; H, 2.08; N, 4.82; Cu, 10.93%.

5, 5'-Dimethoxysalicylaldehyde - ethylenediimine-copper.—(a) It is obtained from yellow 5-methoxysalicylaldehyde-copper as described above. Recrystallization from chloroform gave green plates. $\lambda_{max}^{C_5H_5N}$ 400, 585 mμ[9].

Anal. Found: C, 53.74; H, 4.59; N, 6.77; Cu, 16.91. Calcd. for $C_{18}H_{18}O_4N_2Cu$: C, 54.45; H, 4.65; N, 7.19; Cu, 16.30%.

(b) 5,5'-Dimethoxysalicylaldehyde - ethylene - diimine (600 mg.) in boiling ethanol (80 ml.) was treated with a saturated aqueous solution containing copper acetate (400 mg.) and the mixture was boiled for thirty minutes on a water bath. After cooling, the precipitates were filtered and recrystallized from chloroform.

(c) To an intimate mixture of 5,5'-dihydroxysalicylaldehyde-ethylenediimine-copper (400 mg.) and dimethylsulfate (400 mg.) was added 0.8 ml. of 10% aqueous sodium hydroxide solution; it reacted exothermically at once, stirred thoroughly to complete the reaction. After an hour, the paste was filtered, washed with water, dried and recrystallized from chloroform.

5, 5'-Dihydroxysalicylaldehyde-ethylenediimine-copper.—To a boiling solution of 5,5'-dihydroxysalicylaldehyde-ethylenediimine (1.2 g. in 215 ml. ethanol) was added copper acetate (0.96 g. in 20 ml. water) and the mixture heated for twenty minutes on a water bath. After the mixture was cooled, the precipitate was filtered and recrystallized from ethanol. It showed blue purple as needles but a gray green color appeared when powdered. Yield, 1 g.

Anal. Found: C, 50.15; H, 4.47; N, 6.64; Cu, 17.27. Calcd. for $C_{16}H_{14}N_2O_4Cu$-H_2O: C, 50.61; H, 4.25; N, 7.38; Cu, 16.74%.

Addition Compound with Propionic Acid[9].—*5, 5'-Diiodosalicylaldehyde-ethylenediimine-copper.*

Anal. Found: C, 33.49; H, 2.70; N, 4.53. Calcd. for $C_{16}H_{12}O_2N_2I_2Cu$-$C_3H_6O_2$: C, 34.79; H, 2.77; N, 4.27%.

5, 5' - Dimethoxysalicylaldehyde - ethylenediimine - copper.

Anal. Found: C, 54.20; H, 5.39; N, 6.10. Calcd. for $C_{18}H_{18}O_4N_2Cu$-$C_3H_6O_2$: C, 54.35; H, 5.21; N, 6.04%.

Addition Compounds with Phenol[9].—*5, 5'-Diiodosalicylaldehyde-ethylenediimine-copper.*

Anal. Found: C, 40.16; H, 2.92; N, 4.18. Calcd. for $C_{16}H_{12}O_2N_2I_2Cu$-C_6H_6O: C, 39.09; H, 2.68; N, 4.15%.

5, 5' - Dimethoxysalicylaldehyde - ethylenediimine - copper.

Anal. Found: C, 58.48; H, 4.85; N, 5.63. Calcd. for $C_{18}H_{18}O_4N_2Cu$-C_6H_6O: C, 59.54; H, 5.00; N, 5.79%.

5, 5' - Dibromosalicylaldehyde-ethylenediimine - copper.—The reaction product was purified by washing with benzene or by recrystallization from chloroform containing phenol.

Anal. Found: C, 43.89, H, 2.92; N, 4.74. Calcd. for $C_{16}H_{12}O_2N_2Br_2Cu$-C_6H_6O: C, 45.41; H, 3.12; N, 4.82%.

5, 5' - Dihydroxysalicylaldehyde - ethylenediimine - copper.—The reaction product was purified by washing repeatedly with benzene, and was not recrystallized.

Anal. Found: C, 55.98; H, 4.89; N, 5.00. Calcd. for $C_{16}H_{14}O_4N_2Cu$-C_6H_6O: C, 57.95; H, 4.42; N, 6.15%.

Addition Compounds with Chloroform.—*5, 5'-Dibromosalicylaldehyde-ethylenediimine-copper.*

Anal. Found: C, 36.23, 36.06; H, 2.48, 2.42; N, 5.56, 5.61. Calcd. for $C_{16}H_{12}O_2N_2Br_2Cu$-$\frac{1}{2}CHCl_3$: C, 36.21; H, 2.30; N, 5.12%. Weight decrease at 110°C. Found: 11.13. Calcd. for $C_{16}H_{12}O_2N_2Br_2Cu$-$\frac{1}{2}CHCl_3$: 10.91%.

5, 5'-Diiodosalicylaldehyde-ethylenediimine - copper.—Recrystallized from chloroform.

Anal. Found: C, 28.54; H, 3.35; N, 4.42. Calcd. for $C_{16}H_{12}O_2N_2I_2Cu$-$CHCl_3$: C, 29.13; H, 3.35; N, 4.00%.

Addition Compound with Ethanol.—*5, 5'-Diiodosalicylaldehyde-ethylenediimine-copper.*

Anal. Found: C, 32.43; H, 2.88; N, 4.62. Calcd. for $C_{16}H_{12}O_2N_2I_2Cu$-C_2H_6O: C, 34.44; H, 2.89; N, 4.46%. Weight decrease at 110°C. Found: 6.34. Calcd. for $C_{16}H_{12}O_2N_2I_2Cu$-C_2H_6O: 7.34%.

The author is grateful to Mr. M. Shito and Miss S. Indo for the microanalysis.

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9) Beckman E. P. U. spectrophotometer.

Primary Processes in the Photobleaching of Eosin as Revealed by the Flash Technique

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Shigeo NAGAKI and Masao KOIZUMI

(Received August 17, 1959)

A few years ago, Imamura and Koizumi[1] investigated kinetically the reductive photobleaching of xanthen dyes and proposed a reaction scheme which involved the formation of semiquinone radical with a lifetime of millisecond order. Now, techniques of flash photolysis and flash spectroscopy have been introduced in order to get direct evidence for their conclusion and to obtain more detailed information about the primary processes. The present paper is concerned chiefly with the spectra of the transient intermediates and their assignment along with some discussions about the reaction scheme. A rather remarkable result was that two types of intermediates with a lifetime of millisecond order were observed spectroscopically. One of these was assigned to semiquinone and the other to a certain kind of complex between dye and ethanol.

Experimental

Flash Lamps. — A photolysis flash lamp, six turn helical Terex tube, 10 mm. in diameter, the total length of which was about 1 m., was filled with argon at 4.5 cmHg pressure. It was surrounded by a cylindrical magnesia reflector. A spectroflash lamp was a Terex tube, 20 cm. in length and 15 mm. in diameter, having a flat quartz window, the argon pressure being 20 cmHg. Five 10 μF oil condensers were used for photolysis flash and one condenser of the same capacity for spectroflash, and both of them were charged up to 4 kV. Flashes were triggered by induction coils operated by strobo discharge tubes. The interval of firing was controlled from 0.3 to 700 millisec. by an electronic device. The half height widths of the flashes were measured by an oscilloscope and found to be approximately 60 and <20 μ sec., respectively, a crystal oscillator being used as a time measure.

Spectroscopic.—A Shimazdu QF-60 quartz spectrograph and Fuji Neopan plates were used.

Reaction Vessels. — The vessels were of 10 cm. length and 1 cm. diameter glass tubes with quartz plates cemented on both ends. The glass part of the vessel cuts off shorter wavelengths than 300 mμ.

Materials. — Merck eosin and Wako Pure Chemical Industries G. R. grade ethanol were used. The latter was transparent up to 260 mμ for a 10 cm. path. Throughout the investigation, 1×10^{-5} mol./l. ethanolic solution of eosin was degassed by repeated distillation in high vacuum, sealed in a reaction vessel and then was placed at the center of the helical flash lamp.

Calibration of the Flash Intensity. — Although the flashing condition was made as nearly the same as possible by monitoring the condenser voltage, some variation in intensity could not be avoided. To evaluate correctly the absorption spectra of the transient species from the trace of a microphotometer, the variation of the spectro-flash intensity was taken into account in the following way. From the readings of the trace for the solvent and solution, the logarithm of exposure was determined in the usual way. When the difference in the logarithm of exposure was plotted against the molar extinction coefficient (ε_λ) of eosin, a linear relationship was found to hold in the wavelength region above 480 mμ, where the transient species had no absorption. Since the relation

$$\Delta S_\lambda = \log I_\lambda - \log I'_\lambda + \varepsilon_\lambda cd$$

holds, where ΔS_λ is the difference in logarithm of exposure, I_λ and I'_λ are the intensity of the spectro-flash for solvent and solution, respectively; the intercept of the ordinate gives the value $\log I_\lambda - \log I'_\lambda$, which allows one to calibrate the intensity variation of the spectro-flash.

Results

The absorption spectra are shown in Fig. 1. The spectra of the initial solution were obtained by a Hitachi spectrophotometer EPU-2A. The time interval written is that between the start of the two flashes. As seen from the figure, after 0.6 millisec., the main absorption of eosin decreases to 60% of the initial solution, and at the same time a definite transient absorption comes into existence. Substracting from this the absorbance due to the remaining eosin, the quantity of which

1) M. Koizumi and M. Imamura, This Bulletin, **28**, 117 (1955); **29**, 899 (1956).

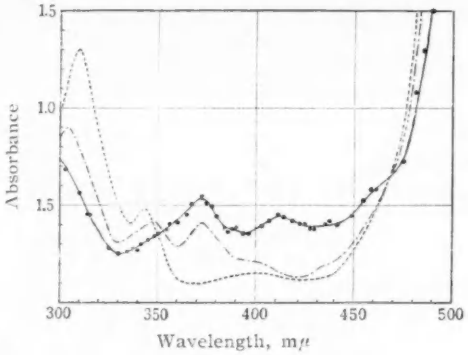

Fig. 1. Transient spectra of eosin.
——: 0.6 millisec.
——: 5 millisec.
----: before flash

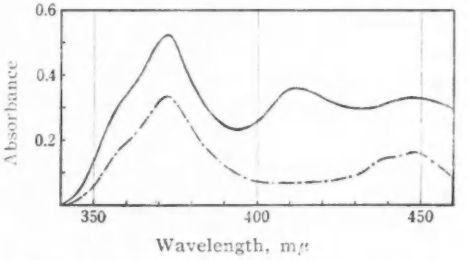

Fig. 2. Absorption spectra of transient species of eosin.
——: 0.6 millisec.
——: 5 millisec.

can be evaluated from the depression of the absorbance in the region longer than 480 mμ, one can obtain the genuine spectra of transient species, which are shown in Fig. 2.

Three peaks are seen at 373, 410 and about 450 mμ. After 5 millisec., the 373 and 450 mμ peaks, which will be called A band from now on, still maintain considerable intensity, whereas the 410 mμ peak (B band) has disappeared. After several minutes, these transient absorption bands thoroughly vanish and the eosin spectra are recovered up to about 88% of the original solution. Twelve per cent loss is attributable, without doubt, to permanent bleaching.

In the presence of air, neither transient spectral change nor permanent bleaching was observed. The deaerated aqueous solution of eosin showed a slight transient depression of eosin absorption spectra,

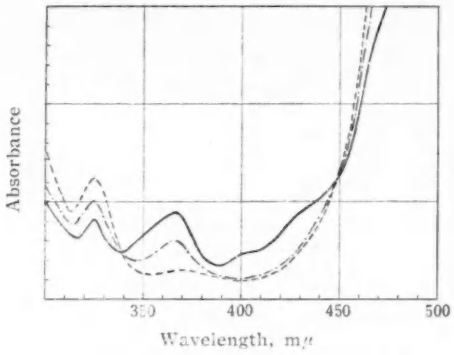

Fig. 3. Transient spectra of uranin.
——: 0.6 millisec.
——: 5 millisec.
----: before flash

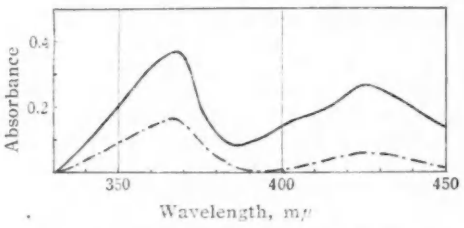

Fig. 4. Absorption spectra of transient species of ulanin.
——: 0.6 millisec.
——: 5 millisec.

but no new spectra were observed in the region of the above mentioned A and B bands.

For uranin in ethanol also, transient spectra were observed by the flash illumination, but at 0.6 millisec. no clear peak corresponding to the 410 mμ peak of eosin was found (Figs. 3 and 4).

It is worth adding here that when only a photolysis flash is fired, a fluorescence spectrum can be taken on a plate, and it is to be noted that the fluorescence intensity varies markedly according to whether the sample is aerobic or not. On the contrary, the measurement by an ordinary fluorimeter (an accessory of the spectrophotometer), shows no such difference.

TABLE I. RELATIVE FLUORESCENCE INTENSITY AT THE PEAK WAVELENGTH

	Flash	Fluorimeter
Aerobic	100	100
In vacuo	5	100

Discussion

The appearance of two spectral bands A and B with different lifetimes indicates that at least two transient species are formed in the initial stage of the reductive photobleaching of eosin.

As regards the assignment of these two bands, there scarcely exists any doubt that the A band is due to the semiquinone radical of eosin on the basis of the kinetic studies of Imamura and Koizumi. The assignment of band B, however, is not so clear-cut. A question may arise whether this absorption is caused by the triplet state of dye, but this possibility can be denied from the following two reasons. The first reason is that the lifetime of the band, being some tenths of a millisecond, would be too long for a triplet. Considered from the results already published in literature, for instance, as reported by Porter et al.[2], triplet states have usually too short a lifetime at room temperature and in ordinary solvents of common fluidity, to be observed by the present apparatus. The second reason is that if it were due to triplet state, the similar band should be observed in aqueous solution because of lower reactivity of water to the triplet state than ethanol, a fact which has been established by kinetic studies of photobleaching[1].

The B band must, therefore, be attributed to some unknown molecular species which perhaps is formed prior to semiquinone. Now, as reported elsewhere[3], the influence of added substances on the bleaching rate of eosin strongly suggests the formation of a certain kind of molecular complex between the excited state of the dye and ethanol. If this scheme is accepted, it is quite natural to attribute the B band to the complex in question.

Furthermore, in order to interpret the other experimental results reported in this paper, it is quite desirable, indeed it seems rather indispensable, to introduce such a complex in the reaction scheme, as will be shown below.

1) From the result that at 0.6 millisec. after the firing of the main flash the quantity of the existent dye drops to about 60% of that of the initial solution, it is very natural to consider that at a certain early period after flashing, nearly all the dye molecules exist as intermediates whose lives are in the order of 10^{-3} sec. or so.

Supposing that a semiquinone is the only one species as such an intermediate, then nearly 50% of dye would be bleached permanently, if one assumes, as is plausible, that semiquinone is stabilized by a dismutation process, $2DH \rightarrow D + DH_2$. Contrary to this expectation, only 12% permanent bleaching is produced by a single flash. In other words, about 24% of the dye is converted into semiquinone by one flash, hence this result necessitates that some other transient species like the complex considered above be existent, and that most of this transient species be deactivated without going to the reaction product.

2) The absence of photobleaching as well as of transient spectrum in aerobic condition is intimately connected with the fact formerly reported, that the reductive photobleaching is completely inhibited by the existence of a very small quantity of oxygen[1]. Imamura and Koizumi who at that time did not conceive of the formation of the complex, estimating the lifetime of the species attacked by oxygen to be 10^{-3} sec. or so from the quantity of oxygen necessary to suppress completely the bleaching reaction, concluded that semiquinone be mainly destroyed by oxygen, rejecting the possibility of the triplet state (with much shorter lifetime) being deactivated. But if so, B band should still be observed in flashing the aerated alcoholic solution. Thus, their scheme is not consistent with the present results and it is necessary to consider that the molecular complex now introduced be deactivated effectively by oxygen.

3) The results of fluorescence measurements are also consistent with the formation of such a complex. Thus by flash illumination in vacuo, a major part of the dye is converted into the complex at an early stage and survives at the end of the flash. Consequently, the illumination has poor efficiency for the fluorescence, since only a little part of dye remains in the ground state throughout the later period of flash. Whereas the complex is rapidly destroyed into its components by the attack of oxygen, yielding the dye molecule in the ground state. This process enables each molecule of dye to emit fluorescence repeatedly many times in the duration of the flash, resulting in a large increase of the fluorescence intensity. Such a situation is not expected if one assumes that

2) Cf. N. K. Bridge and G. Porter, *Proc. Roy. Soc.*, **A244**, 259 (1958).
3) K. Uchida, S. Kato and M. Koizumi, This Bulletin, **33**, 169 (1960).

oxygen mainly attacks the semiquinone radical. In measurements by an ordinary fluorimeter on the other hand, the low intensity of exciting light causes almost no change in the population of the ground state irrespective of whether a sample is free from air or not, hence the same fluorescence intensity results in the two cases.

The above qualitative discussion, though it seems quite plausible, is in fact not conclusive so long as only the fluorescence experiments for ethanol solutions are concerned, because the results are equally well interpreted if one assumes that the triplet state instead of the complex is efficiently deactivated by oxygen. The problem will be clarified if a quantitative comparison is made for the fluorescence intensity of the evacuated and aerated aqueous solution, where neither semiquinone nor complex is formed. At the present stage of investigation, the complex-decomposition-scheme may be said, in view of the discussion in 2), to be more plausible than the triplet state-deactivation-scheme, although the latter process may perhaps take place to some extent.

Summarizing the above discussion one can conclude the following reaction scheme for the reductive photo-bleaching of eosin.

$$D + h\nu \rightarrow D^* \quad (1)$$

$$D^* \rightarrow D + h\nu' \quad (2)$$

$$D^* \rightarrow D^t \quad (3)$$

$$D^t + RH \rightarrow X \quad (4)$$

$$X \rightarrow D + RH \quad (5)$$

$$X \rightarrow DH\cdot + R\cdot \quad (6)$$

$$2DH\cdot \rightarrow D + DH_2 \quad (7)$$

In the presence of air

$$X + O_2 \rightarrow D + RH + O_2 \quad (8)$$

and in addition to reaction 8, perhaps, D^t may also be deactivated to a lesser extent. The process of reaction 8 is faster than reaction 5 or 6 even when the oxygen content is very small.

For uranin also, a similar scheme may hold, but the lifetime of X seems to be much shorter.

Summary

Reductive photobleaching of eosin and uranin in ethanol solutions was studied by the flash technique. Transient spectra of semiquinone with a lifetime of millisecond order was established. In addition, another transient spectra with a life of the same order was observed in the case of eosin. This was interpreted to be due to a certain complex intermediate between ethanol and eosin, formed prior to semiquinone. The aerated alcoholic solution and the evacuated aqueous solution, when illuminated by a flash, showed no transient spectra in the wavelength region of the above two intermediates. The fluorescence of the aerated ethanol solution produced by the flash had about twenty times as large intensity as that of the evacuated solution induced under otherwise similar condition. A scheme for the primary processes of the reductive photobleaching involving the above complex can interpret all these results satisfactorily.

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Studies on Antibiotics and Related Substances. IX. Synthesis of Methyl 5-Methylenecyclopentanone-2-acetate, an Antitumor Substance and Related Compounds

By Sumio UMEZAWA and Mitsuhiro KINOSHITA

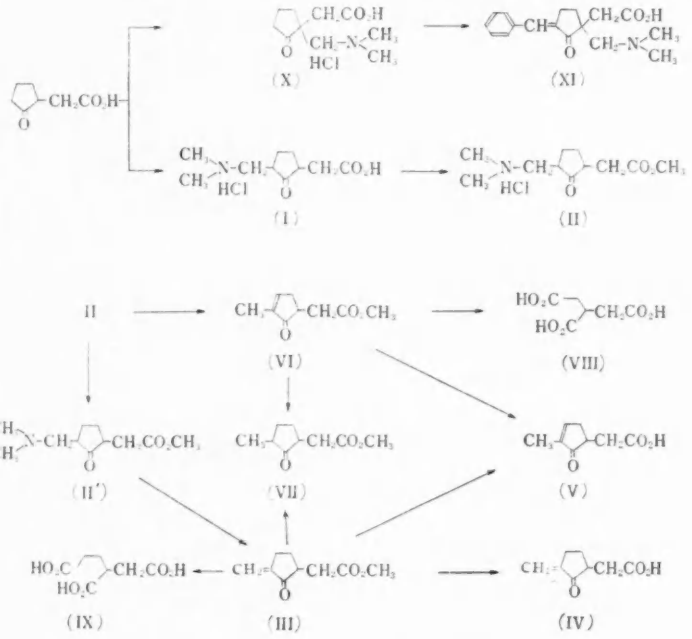
(Received September 3, 1959)

Recent publication[1] from this laboratory described the syntheses and antitumor activities of the methylene derivatives of cyclopentanone-3-carboxylic acid, relating to sarkomycin[2], an antitumor antibiotic. The present paper is concerned with an extention of this work in which the syntheses and antitumor activities of 5-methylenecyclopentanone-2-acetic acid and its ester are described.

Cyclopentanone-2-acetic acid was prepared by the Linstead and Meade's method[3]. A mixture of cyclopentanone-2-acetic acid, paraformaldehyde and dimethylamine hydrochloride was fused to give two kinds of Mannich base hydrochlorides; 2-(dimethylaminomethyl)cyclopentanone-2-acetic acid hydrochloride (X) crystallized at first from the absolute ethanol solution of the reaction mixture and 5-dimethylaminomethyl isomer (I), the desired product, was obtained from the mother liquor in a 24.2% yield.

On treating with benzaldehyde in the presence of sodium hydroxide, the 2-dimethylaminomethyl isomer (X) afforded a benzylidene derivative (XI), indicating[4] the presence of an activated methylene group in VIII.

Thermal decomposition of the methyl



1) S. Umezawa and M. Kinoshita, This Bulletin, **30**, 267 (1957); ibid., **32**, 223 (1959).

2) H. Umezawa, T. Yamamoto, T. Takeuchi, T. Okami, S. Yamaoka, T. Okuda, K. Nitta, K. Yagishita, R. Utahara and S. Umezawa, *Antibiotics & Chemotherapy*, **4**, 514 (1954).

3) R. P. Linstead E. M. Meade, *J. Chem. Soc.*, **1934**, 940.

4) Benzaldehyde condenses readily on the two activated methylene groups of cyclopentanone; C. Mentzel, *Ber.*, **36**, 1499 (1903); R. Cornubert, *Compt. rend.*, **190**, 440 (1930).

ester (II) of 5-dimethylaminomethyl isomer (I) afforded a colorless oil (48%) which gave analyses for $C_9H_{12}O_3$ but had neither antitumor nor antibacterial activity. The product contained a carbonyl group as shown by the formation of a semicarbazone of m. p. 162~163°C. The ultraviolet absorption suggested the presence of an α,β-unsaturated carbonyl group, showing maxima at 228 and 307 mμ and the infrared spectrum also indicated a conjugated carbonyl system (Figs. 1 and 2). Ozonolysis yielded tricarballylic acid (VIII) but no formaldehyde. These data led to the conclusion that the destructive distillation of II produced a rearrangement of the exocyclic double bond formed by elimination of dimethylamine to a more stable conjugated system to give methyl 5-methyl-4-cyclopenten-1-one-2-acetate (VI).

When the free base (II') obtained from II by treatment with ammonia in chloroform was subjected to destructive distillation, the desired methyl ester (III) of 5-methylenecyclopentanone-2-acetic acid was obtained in a 42.7% yield.

Acid hydrolysis of III with 5% hydrochloric acid-acetone solution produced a rearrangement of exocyclic double bond as well as hydrolysis, giving 5-methyl-4-cyclopenten-1-one-2-acetic acid (V) which was found to be identical with the product obtained from VI by alkaline hydrolysis, as judged by mixed melting point determination and by comparison of ultraviolet and infrared absorption spectra. Hydrogenation of III with platinum catalyst in methanol solution afforded methyl 5-methylcyclopentanone-2-acetate (VII); the semicarbazone, m. p. 149~149.5°C, of VII was found to be identical with the semicarbazone of the product obtained from VI by catalytic hydrogenation, as judged by mixed melting point determination. Ozonolysis of III gave formaldehyde (isolated as the methone derivative) and butane-1, 2, 4-tricarboxylic acid (IX); formation of the former established the presence of an exomethylene group in III.

The infrared absorption spectrum of III indicated a conjugated carbonyl system and the ultraviolet absorption data also suggested the presence of the α,β-unsaturated carbonyl group, showing maxima at 232 and 333 mμ (Figs. 1 and 3). The accumulated data provided definite proof that the decomposition product III from the free base of II was methyl 5-methylenecyclopentanone-2-acetate.

Mild hydrolysis of III with dilute sulfuric acid followed by extraction with ethyl acetate and evaporation of the solvent in vacuo gave a 16.8% yield of a crude product of 5-methylenecyclopentanone-2-acetic acid

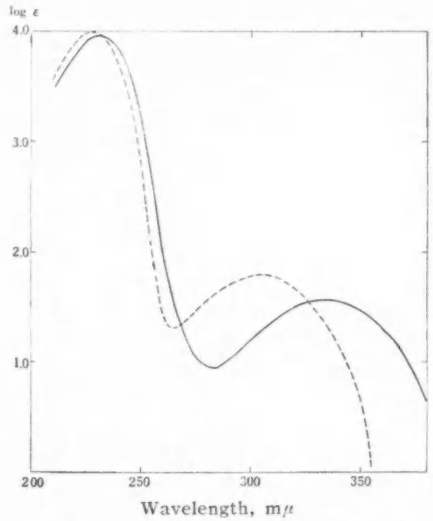


Fig. 1. Ultraviolet absorption spectra of methyl 5-methylenecyclopentanone-2-acetate (——) and methyl 5-methyl-4-cyclopenten-1-one-2-acetate (----) in methanol.

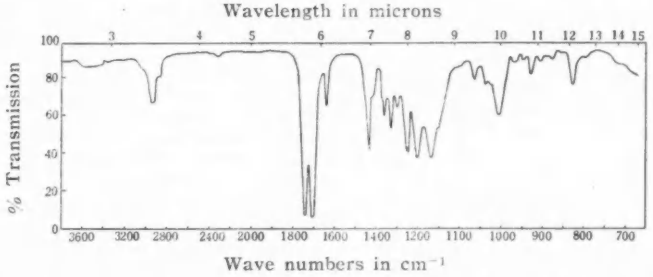


Fig. 2. Infrared absorption spectrum of methyl 5-methyl-4-cyclopenten-1-one-2-acetate (liquid).

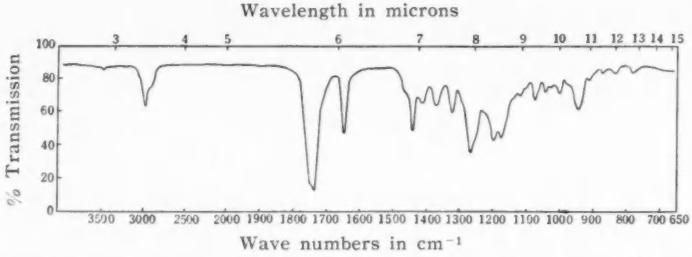


Fig. 3. Infrared absorption spectrum of methyl 5-methylenecyclopentanone-2-acetate (liquid).

(IV), a pale yellow, viscous liquid, which spontaneously polymerized so readily that further purification could not be accomplished. With the crude product, absorptions in the infrared spectrum indicated a conjugated carbonyl system, and the ultraviolet absorption data also suggested the presence of the α,β-unsaturated cabonyl group, showing a maximum at 230 mμ.

Both 5-methylenecyclopentanone-2-acetic acid and its ester (III) were found to possess antitumor and antimicrobial activities. As in the case of 5-methylenecyclopentanone-3-carboxylic acid[1], the methyl ester (III) was more potent than the corresponding free acid (IV).

Experimental

2-(Dimethylaminomethyl)cyclopentanone-2-acetic Acid Hydrochloride (X). — A mixture of cyclopentanone-2-acetic acid[4] (14.2 g.) and dimethylamine hydrochloride (8.2 g.) was heated to 75°C. To the resulting melt was added paraformaldehyde (3.0 g.) and the mixture stirred at 75°C for 3 hr. and evaporated in vacuo to remove moisture. The resulting syrup was dissolved in hot absolute ethanol and filtered. After cooling, some seeds of pure X were added to the filtrate and the mixture was stored in an ice box. The first crystalline crop was separated, and washed with acetone-ethanol (3 : 1). The product (5.5 g.) was triturated with hot absolute ethanol (10 cc.). After standing at room temperature, filtration followed by washing with cold ethanol (5 cc.) gave 3.4 g. (14.4%) of 2-(dimethylaminomethyl)-cyclopentanone-2-acetic acid hydrochloride (X), m. p. 145~147°C (decomp.). An analytical sample was obtained by recrystallization from methanol, m. p. 150~150.7°C (decomp.).

Anal. Found: C, 51.05; H, 7.42; N, 5.72. Calcd. for $C_{10}H_{15}O_3NCl$: C, 50.95; H, 7.64; N, 5.95%.

5-Benzylidene-2-(dimethylaminomethyl)cyclopentanone-2-acetic Acid (XI). — To a solution of 2-(dimethylaminomethyl) cyclopentanone-2-acetic acid hydrochloride (X) (200 mg.) in 2.5 N sodium hydroxide (1.6 cc.) was added benzaldehyde (100 mg.) and the mixture stirred at 20°C for one hour. The resulting yellow solution was adjusted to pH 3 with 3 N hydrochloric acid, and shaken with ether. The water-layer was evaporated to dryness in vacuo and then extracted with absolute ethanol. Evaporation of ethanol solution afforded a crude hydrochloride of XI, very hygroscopic yellow amorphous powder; yield, 210 mg. (77%); characteristic strong absorption in ultraviolet spectrum at λ_{max}^{MeOH} 308~309 mμ ($E_{1cm}^{1\%}$ 304). To a solution of the crude hydrochloride (200 mg.) in methanol (1.6 cc.) was added picric acid (200 mg.) in hot methanol (2.4 cc.). Water was added until the solution appeared turbid, and the mixture was allowed to stand overnight in a refrigerator to afford short prisms of picrate of XI; yield, 183 mg. (42% based on the crude hydrochloride of XI), m. p. 149~150°C (decomp.). Two recrystallizations from methanol-water gave a pure sample, m. p. 150~151°C (decomp.).

Anal. Found: C, 53.65; H, 4.45; N, 10.82. Calcd. for $C_{23}H_{24}O_{10}N_4$: C, 53.49; H, 4.68; N, 10.85%.

5-(Dimethylaminomethyl)cyclopentanone-2-acetic Acid Hydrochloride (I). — The mother liquor of the above-mentioned first crop (X) was stored in an ice box for 3 days to afford the second crop, which was collected, washed with acetone-ethanol (3 : 1) and dried; yield, 6.6 g.; m. p. 130~135°C (decomp.). Recrystallization from ethanol-acetone gave 5.6 g. of 5-(dimethylaminomethyl)cyclopentanone-2-acetic acid hydrochloride (I) (24.2%), m. p. 135~137°C (decomp). An analytical sample was obtained by recrystallization from methanol, m. p. 137~138.5°C (decomp.).

Anal. Found: C, 51.31; H, 7.56; N, 6.08. Calcd. for $C_{10}H_{18}O_3NCl$: C, 50.95, H, 7.64; N, 5.95%.

Methyl 5-(Dimethylaminomethyl)cyclopentanone-2-acetate Hydrochloride (II). — A mixture of 5-(dimethylaminomethyl)cyclopentanone-2-acetic acid (I) (6.1 g.) and absolute methanol (60 cc.) was saturated with dry hydrogen chloride and allowed to stand overnight. The solvent was removed by distillation at about 40°C in vacuo and the residue was dried in vacuo over phosphorus pentoxide. The resulting crystals were dissolved in a small quantity of absolute methanol by warming and the solution was diluted with absolute ether, whereupon there separated a crystalline precipitate of methyl 5-(dimethylaminomethyl)cyclopentanone-2-acetate hydrochloride (II), m. p. 117~121°C. Yield, 6.0 g. (93%). Two recrystallizations from methanol-ether, m. p. 123.5~124.5°C.

Anal. Found: C, 52.54; H, 7.87; N, 5.76. Calcd. for $C_{11}H_{20}O_3NCl$: C, 52.88; H, 8.07; N, 5.61%.

Methyl 5-Methylenecyclopentanone-2-acetate (III). — To a solution of methyl 5-(dimethylaminomethyl)cyclopentanone-2-acetate hydrochloride (II) (3.0 g.) in chloroform (10 cc.) was added saturated ammonia-chloroform solution (6.3 cc.), whereupon ammonium chloride immediately precipitated. The chloroform-layer was separated and concentrated under reduced pressure. The residue was heated at 108°C in an oil bath under highly reduced pressure (0.1~0.01 mmHg). Colorless distillate (1.4 g.), which was collected in a receiver cooled in a dry ice-methanol bath, was dissolved in ether (6.5 cc.) and shaken with dilute hydrochloric acid to remove dimethylamine and unreacted free amine-ester (II'). The ether-layer was dried over anhydrous sodium sulfate, and the solvent was removed in vacuo to afford a crude product of methyl 5-methylenecyclopentanone-2-acetate (III) (810 mg., 42.7%). Vacuum distillation of the crude product gave a low yield of pure sample of III, b. p. 60~65°C (bath temp.)/0.01 mmHg. There was much residue in the distillation flask, indicating the ready polymerization of III.

Absorption spectra: ultraviolet, λ_{max}^{MeOH} 232 (ε 9100) and 333 mμ (ε 36.9); infrared, ν_{max}^{liq} 1733 (ester and conjugated carbonyl) and 1643 cm^{-1} (C=C).

Anal. Found: C, 63.81; H, 7.16. Calcd. for $C_9H_{12}O_3$: C, 64.27; H, 7.19%.

Catalytic Hydrogenation of III. — A solution of freshly prepared III (300 mg.) in methanol (3 cc.) was shaken with platinum oxide (24 mg.) and hydrogen; 44 cc. (11°C, 766.1 mmHg, 95% based on theoretical amount) of hydrogen was absorbed in 18 min. The mixture was filtered and concentrated under reduced pressure and distilled in vacuo to give methyl 5-methylcyclopentanone-2-acetate (VII) (235 mg., 77.6%), b. p. 62°C (bath temp.)/0.01 mmHg.

Anal. Found: C, 63.84; H, 8.63. Calcd. for $C_9H_{14}O_3$: C, 63.51; H, 8.29%.

Semicarbazone of methyl 5-methylcyclopentanone-2-acetate; colorless needle from ethyl acetate, m. p. 149~149.5°C.

Anal. Found: C, 52.95; H, 7.37; N, 18.63. Calcd. for $C_{10}H_{17}O_3N_3$: C, 52.85; H, 7.54; N, 18.49%.

Ozonolysis of III. — a) A solution of 100 mg. of III in ethyl acetate (5 cc.) was treated with an approximately 2% (by weight) ozone-oxygen mixture at 0°C at a rate of 500cc./min. for 2 hr. The resulting solution was mixed with water (5 cc.) and zinc dust (150 mg.) and the mixture was refluxed for 30 min. The reaction mixture was filtered while hot into a solution of methone (150 mg.) in 5 cc. of ethanol. Dilution with 10 cc. of water afforded the needles of formaldehyde methone, m. p. 185~187°C. Recrystallization from methanol-water; m. p. 188~189°C; yield, 30 mg. Admixing with an authentic specimen of formaldehyde methone showed no change of melting point.

b) A solution of 300 mg. of freshly prepared III in ethyl acetate (14 cc.) was treated with ozone as mentioned above a) at −15°C. The resulting yellow solution was concentrated in vacuo below 10°C to afford a viscous yellow oil, which was heated with 1.6 cc. of 30% hydrogen peroxide at 90°C for one hour. The colorless solution was evaporated under reduced pressure. Addition of water to the residue followed by evaporation was repeated to remove excess of hydrogen peroxide. The final residue was refluxed with 3.5 cc. of 10% methanolic potassium hydroxide for 2 hr. Methanol was removed, acidified to pH 2.4 with dilute hydrochloric acid, saturated with ammonium sulfate and extracted with ether continuously for 3 hr. After the extract was dried over anhydrous sodium sulfate, the ether was distilled off. The residue immediately crystallized; yield, 200 mg. (59%); m. p. 108~112°C. A paper chromatography of this product with xylene-phenol-85% formic acid (7 : 3 : 1) showed only the distinct spot which had the same R_f value as that of an authentic butane-1,2,4-tricarboxylic acid[5] (IX). Recrystallization from ethyl acetate gave 51 mg. of pure butane-1,2,4-tricarboxylic acid, m. p. 119.5~120.8°C, mixed m. p. 120~120.8°C.

5-Methylenecyclopentanone-2-acetic Acid (IV). — A mixture of freshly prepared methyl 5-methylenecyclopentanone-2-acetate (III) (994 mg.) and 1.5 N sulfuric acid (20 cc.) was stirred at 28~32°C for 2.5 hr. After removal of a considerable amount of resinous material (527 mg.) by decantation, the resulting solution was adjusted to pH 8.0 with a saturated solution of sodium bicarbonate, and shaken with two 15 cc. portions of ether to remove any unchanged ester. The water-layer was adjusted to pH 2.4 with 1.5 N sulfuric acid and extracted with two 15 cc. portions of ethyl acetate. After the extract was dried over anhydrous sodium sulfate, the ethyl acetate was removed by distillation in vacuo at about 0°C to yield a crude product of IV, a pale yellow viscous oil; yield, 153 mg. (16.8%). The freshly prepared sample was soluble in water and methanol. However, on standing at room temperature, the product rapidly polymerized and became much less soluble in water and methanol. It resisted attempts to recrystallize it. The ultraviolet absorption spectrum of the product showed a strong absorption at 230 mμ ($E_{1cm}^{1\%}$ 197) in methanol, indicating the presence of an α,β-unsaturated ketone group. Infrared spectrum in liquid showed maxima at 1735 (carboxyl and conjugated carbonyl), 1642 (C=C) and 2700~2500 cm^{-1} (carboxyl OH).

5-Methyl-4-cyclopenten-1-one-2-acetic Acid (V). — a) A mixture of methyl 5-methyl-4-cyclopenten-1-one-2-acetate (VI) (200 mg.) and 10% sodium hydroxide solution (0.45 cc.) was stirred at 17°C for one hour. The resulting solution was acidified to pH 2.0 by addition of dilute hydrochloric acid, saturated with ammonium sulfate, and extracted with three 1 cc. portions of ether. The dried extract was concentrated to afford a pale yellow oil (160 mg.) which, on standing, slowly

5) This was prepared by the method of Tawney and Prill: P. O. Tawney and E. J. Prill, *J. Am. Chem. Soc.*, **70**, 2828 (1948).

turned to a solid mass of crystals intermixed with oil. The crude crystals were drained on porous porcelain to remove an oily material; yield, 50 mg. (27%), m. p. 43~47°C. A pure sample of 5-methyl-4-cyclopenten-1-one-2-acetic acid (V) was obtained by recrystallization from ether-benzine, colorless prism, m. p. 48~49°C.

Absorption spectra: Ultraviolet, λ_{max}^{MeOH} 228~229 (ε 9850) and 310 mμ (ε 48.4); infrared, ν_{max}^{Nujol} 1670 (conjugated carbonyl), 1630 (C=C), 2700~2500 (carboxyl OH) and 1738 cm^{-1} (carboxyl C=O).

Anal. Found: C, 62.21; H, 6.69. Calcd. for $C_8H_{10}O_3$: C, 62.32; H, 6.54%.

b) A solution of freshly prepared methyl 5-methylenecyclopentanone-2-acetate (III) (1.4 g.) in 14.5 cc. of acetone-hydrochloric acid mixture (6 : 1 by weight) was allowed to stand at 20°C for 10 hr. To a resulting solution, water (30 cc.) and sodium bicarbonate (3 g.) were added under ice-cooling. After removal of acetone under reduced pressure below 5°C, the aqueous layer was extracted with two 10 cc. portions of ether, acidified to pH 2.4 with 3 N hydrochloric acid and again extracted with three 10 cc. portions of ethyl acetate. The dried ethyl acetate solution was concentrated under reduced pressure to afford a pale yellow oil (560 mg.) which crystallized gradually on standing. Treatment on a porous porcelain gave crude crystals (70 mg.), which was recrystallized from ether-benzine, m. p. 48~49°C and mixed m. p. with V obtained in a) 48~49°C. The ethereal extract was concentrated, and then treated in the same manner as described above in a) to afford a viscous oil (500 mg.). Distillation gave a fraction (70 mg.) of b. p. 125~128°C (bath temp.)/0.005 mmHg, which crystallized immediately. Recrystallization from ether-benzine yielded a pure sample of V, m. p. and mixed m. p. 48~49°C.

Methyl 5-Methyl-4-cyclopenten-1-one-2-acetate (VI). — Methyl 5-(dimethylaminomethyl)cyclopentanone-2-acetate hydrochloride (II) (1.0 g.) was placed in a round-bottom flask and heated in an oil bath at 150°C for 15 min. The resulting orange colored product was cautiously distilled at 150°C/0.01 mmHg to afford a colorless liquid (VI) in a receiver cooled in a dry ice-methanol bath. By redistillation of the liquid, pure sample of VI was obtained; yield, 325 mg. (48%); b. p. (bath temp.) 80°C/0.01 mmHg.

Absorption spectra: Ultraviolet, λ_{max}^{MeOH} 228 mμ (ε 9750) and 307 mμ (ε 62.7); infrared, ν_{max}^{liq} 1712 (conjugated carbonyl), 1640 (C=C) and 1745 cm^{-1} (ester C=O).

Anal. Found: C, 63.85; H, 7.41. Calcd. for $C_9H_{12}O_3$: C, 64.27; H, 7.19%.

Semicarbazone of VI; colorless needles, m. p. 162~163°C.

Anal. Found: C, 53.15; H, 6.49; N, 18.45. Calcd. for $C_{10}H_{15}O_3N_3$: C, 53.25; H, 6.72; N, 18.64%.

Catalytic Hydrogenation of VI. — A sample (300 mg.) in methanol (3 cc.) absorbed theoretical amount of hydrogen in the presence of platinum oxide (24 mg.) in 12 min. The reduced product was purified by distillation under reduced pressure to give methyl 5-methylcyclopentanone-2-acetate (VII) (282 mg., 93%), b. p. (bath temp.) 85~89°C/0.03 mmHg. The sample readily afforded a *semicarbazone*, m. p. 149~149.5°C, which did not depress the melting point of the corresponding derivative of the hydrogenation product of III.

Ozonolysis of VI was carried out in the same manner as described in the ozonolysis of III: a) The compound (200 mg.) did not give any formaldehyde methone, indicating the absence of a terminal methylene group. b) The compound (200 mg.) gave a crude crystalline product (117 mg. 56%) which afforded only the distinct spot of tricarballylic acid (VIII) by paper chromatography. Recrystallization from ether gave pure tricarballylic acid; m. p. and mixed m. p. 161~162°C.

Bioassays. — Preliminary results have indicated that methyl 5-methylenecyclopentanone-2-acetate (III) completely inhibits the growth of *M. pyogenes var. aureus* 209-p, *E. coli*, *Saccharomyces sake* and *Penicillium* 408,701 in a dilution of 1 : 16000. 5-Methylenecyclopentanone-2-acetic acid (IV) completely inhibited the growth of *Trichophyton mentagrophytes* in a dilution of 1 : 32000, but had comparatively weak activities against other fungi and bacteria tested.

5-Methyl-4-cyclopenten-1-one-2-acetate had no antimicrobial and antitumor activity, as expected from the fact that 2-methyl-2-cyclopenten-1-one-3-carboxylic acid obtained from sarkomycin (2-methylenecyclopentanone-3-carboxylic acid) by thermal isomerization had no biological activity[6].

It is interesting to find that III and IV possess antitumor activity[7]. The minimum necessary concentrations of III and IV for the anti-HeLa-cell effect were 15.6 and 125 μg/cc.

A detailed report on the biological activities of III and IV will be published elsewhere.

Summary

1) 5-(Dimethylaminomethyl)cyclopentanone-2-acetic acid hydrochloride (I) and 2-dimethylaminomethyl isomer (X) have been synthesized from cyclopentanone-2-acetic acid by means of the Mannich reaction.

2) Methyl 5-(dimethylaminomethyl) cyclopentanone-2-acetate (II′) has been degraded to give methyl 5-methylenecyclopentanone-2-acetate (III), which has been hydrolyzed into 5-methylenecyclopentanone-2-acetic acid (IV), a homologue of isosarkomycin.

3) Destructive distillation of the hydrochloride (I) afforded methyl 5-methyl-4-cyclopenten-1-one-2-acetate(VI), an isomer of III.

6) I. R. Hooper, L. C. Cheney, M. J. Cron, O. B. Fardig, D. A. Johnson, D. I. Johnson, F. M. Palermiti, H. Schmitz and W. B. Wheatley, *Antibiotics & Chemotherapy*, **5**, 590 (1955).

7) Private communication from Prof. H. Umezawa of National Institute of Health, Tokyo.

4) It has been found that III and IV possess antitumor and antimicrobial activities.

The authors are indebted to Professor H. Umezawa, National Institute of Health, Tokyo, for antitumor assays.

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SHORT COMMUNICATIONS

Chemical Structure of Miliacin

By Shokichi Abe

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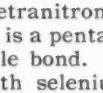
A crystalline substance (I, $C_{31}H_{52}O$, m.p. 282°C, $[\alpha]_D$+8.0°) was isolated from *Panicum miliaceum L.* and from *Syntherisma sanguinalis Dulac var. calialis Honda* by Ito[1] and was named miliacin.

Its ultraviolet absorption spectrum did not indicate the presence of conjugated double bond system, but the color reaction with tetranitromethane suggested the presence of double bond. From its infrared absorption spectrum (9.0 μ) its oxygen linkage was supposed to be an ether type. The oxidation product, miliacin oxide (II, $C_{31}H_{52}O_2$, m.p. 285.5~286°C, $[\alpha]_D$+52.3°) was obtained by the action of perbenzoic acid in chloroform, this oxide did not show the color reaction with tetranitromethane. It follows that miliacin is a pentacyclic compound having a double bond.

Upon oxidation with selenium dioxide, miliacin and miliacin oxide afforded a diendione (III, $C_{31}H_{46}O_3$, m.p. 253°C, $[\alpha]_D$−87.6°, λ_{max} 281 mμ log ε 4.2), whose infrared absorption spectrum (9.0 μ) revealed the existence of the ether linkage. The ultraviolet absorption spectrum of this compound was similar to that of β-amyradiendionol. This fact means that this compound contains a partial structure,  , characteristic of compound derived from β-amyrin-oleanane series. Therefore, it may be concluded that miliacin is a member of β-amyrin-oleanane series and its ester linkage does not participate with the carbon atoms at positions 9, 11—13, 18 and 19.

Upon treatment with hydrogen chloride in chloroform, miliacin oxide afforded compound (IV, $C_{31}H_{50}O$, m.p. 210~211°C, $[\alpha]_D$ −63.0°, λ_{max} 243 mμ log ε 4.3, 250 mμ log ε 4.4, 260 mμ log ε 4.2). Its infrared (9.0 μ) and ultraviolet absorption spectrum and optical rotation difference suggested the presence of an ether linkage and $\Delta^{11:13(18)}$ conjugated double bond. On the other hand, miliacin was changed to its isomer (V, $C_{31}H_{52}O$, m.p. 189°C, $[\alpha]_D$−23.4°) by the same treatment. This isomer gave an oxide (VI, $C_{31}H_{52}O_2$, m.p. 262°C, $[\alpha]_D$+42.7°), which showed no color reaction with tetranitromethane. From the infrared absorption spectrum and the optical rotation difference of this isomer, it was assumed that the double bond of miliacin had rearranged to $\Delta^{13(18)}$ by this treatment.

By the action of boron trifluoride-acetic acid or *p*-toluenesulfonic acid in acetic anhydride-acetic acid, miliacin afforded a diene hydrocarbon (VII, $C_{30}H_{48}$, m.p. 125°C, $[\alpha]_D$+41.2°), which gave a dioxide (VIII, $C_{30}H_{48}O_2$, m.p. 203°C, $[\alpha]_D$+73.5°) by the oxidation with perbenzoic acid. This diene was prepared by David[2] from germanicol and has the structure 8:10:14-trimethylnovoleana-3(5):8-diene. By the action of *p*-toluenesulfonic acid miliacin oxide gave 5:8:14-trimethylnovoleana-9(10):11:13(18)-triene[3] (IX, $C_{30}H_{46}$, m.p. 137°C).

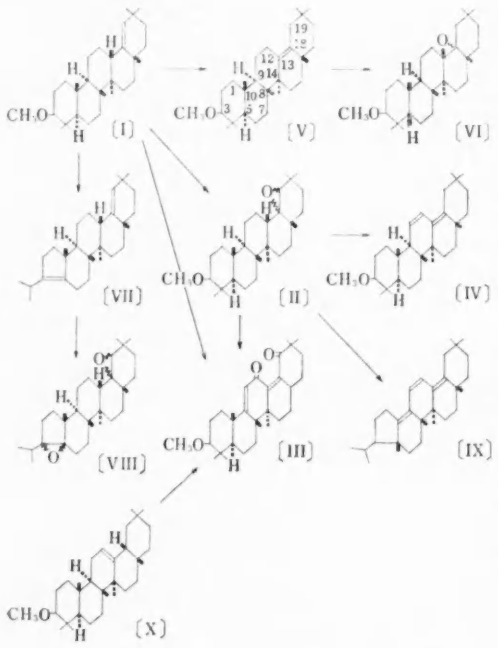
1) H. Ito, *J. Faculty Agr. Hokkaido Imp. Univ.*, **37**, 1 (1934); *J. Chem. Soc. Japan (Nippon Kwagaku Kwaishi)*, **59**, 274 (1938).

2) S. David, *Bull. soc. chim. France*, **1949**, 427.

3) G. G. Allan, M. B. E. Fayez, F. S. Spring and R. Stevenson, *J. Chem. Soc.*, **1956**, 456.

Isosawamilletin[4] (X, 3β-methoxyolean-12-ene) was oxidized with selenium dioxide to a diendione, which was identical with compound III.

It was deduced from the foregoing experimental results that miliacin was 3β-methoxygermanicene (I, 3β-methoxyolean-18-ene), the conjugated diene was 3β-methoxyoleana-11 : 13(18)-diene [IV], and the isomer derived from miliacin by the action of hydrogen chloride was 3β-methoxyolean-13(18)-ene [V], as indicated in the next figure.



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4) T. Obara and S. Abe, *Bull. Agr. Chem. Soc. Japan*, **21**, 388 (1957); I. M. Morice and J. C. E. Simpson, *J. Chem. Soc.*, **1942**, 198.

*On the Model Form of the Catalytic Wave of Proteins**

By Mutsuaki Shinagawa
and Hiroyuki Nezu

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In order to extend the knowledge about the nature of the catalytic wave of protein[1,2] a model experiment was undertaken, and the following three points were emphasized in this experiment: 1) hydrogen sulfide and cystine were used as typical sulfhydryl compounds; 2) the influence of methyl cellulose and gelatin on the catalytic wave of cystine was examined polarographically; and 3) the influence of glucose, sucrose, glucosamine and glycogen on the cystine wave was similarly examined. In the latter case, these sugars were used as model compounds for the carbohydrates contained in the mucoprotein molecule, which is said to be an effective substance for the demonstration of the serum filtrate.

From such experiments, the various wave patterns analogous to those of the protein wave were obtained by regulating the amounts of each of the constituents in the test solutions (Table I).

Single Rounded Cystine-like Wave.—Hydrogen sulfide, which may be considered as one of the simplest of the sulfhydryl compounds, was examined polarographically over a large range of concentrations in the buffered cobaltous solutions, i.e. 0.1 M NH_4OH, 0.1 M NH_4Cl and 10^{-3} M $CoCl_2$. When hydrogen sulfide was added to the solution containing gelatin, the single rounded wave analogous to the cystine wave appeared and the diffusion current of cobalt disappeared. When hydrogen sulfide was added to the solution, and then gelatin was added, the single rounded wave did not appear. If the solution contains large amounts of gelatin, the wave analogous to that of cystine did not appear and the diffusion current of cobalt disappeared (Fig. 1A). This cystine-like wave was observed even at the limiting concentrations of hydrogen sulfide as low as 10^{-7} M.

* Presented at the Polarographic Discussion Meeting, Kyoto, October, 1957.

1) R. Brdicka, *Research (London)*, **1**, 25—35 (1948).

2) M. Brezina and P. Zuman, "Die Polarographie in der Medizin, Biochemie und Pharmazie", Akademische Verlagsgeselleschaft, Leipzig (1956), pp. 532—618.

TABLE I. POLAROGRAPHIC EFFECTS OF GELATIN AND CARBOHYDRATES ON THE CATALYTIC WAVE OF HYDROGEN SULFIDE AND CYSTINE IN THE AMMONIACAL BUFFERED COBALTOUS SOLUTION

Case	Geratin	Carbo-hydrate	Sulfhydryl compound	Single wave (or 2nd wave), V.	Double wave	Unknown wave, V.
1	—	—	H	—	—	—
2	G	—	H	−1.6	—	−0.95
3	G	—	H	—	—	—
4	—	M	H	−1.6	—	−0.7
5	—	Gl	H	−1.6	—	−0.7
6	—	—	C	poorly defined	—	—
7	G	—	C	−1.75	—	−1.0
8	—	M	C	−1.75	well defined	−1.0
9	G	M	C	−1.75	well defined	−1.0
10	—	Gl	C	−1.75	poorly defined	−1.0
11	—	S	C	−1.75	poorly defined	−1.0
12	—	Gs	C	−1.75	poorly defined	−1.0
13	—	Gg	C	−1.75	poorly defined	−1.0

C: 10^{-3} M Cystine Gl: 0.1% Glucose M: 0.1% Methyl cellulose
G: 0.1% Gelatin Gs: 0.1% Glucosamine S: 0.1% Sucrose
Gg: 0.1% Glycogen H: Hydrogen sulfide

Protein-like Wave.—When methyl cellulose was added to the buffered cobaltous solution, the polarographic double wave similar to the protein double wave appeared as shown Fig. 1B. Other carbohydrates such as glucose, sucrose, glucosamine and glycogen were examined in order to determine whether their activities were similar to that of methyl cellulose on the formation of the wave analogous to the protein wave (Table I). Further quantitative experiments were initiated in order to examine the influence of methyl cellulose and gelatin on the cystine wave (Fig. 2).

It seems that Brdicka's mechanism[3], generally accepted since 1933, is unsatisfactory to explain these phenomena for the following reasons: 1) It might be difficult to supply hydrogen ions to the electrode surface from the bulk of an ammoniacal buffered solution at about pH 9. 2) At a potential of about −1.6 V. where the two peaks of the double wave appear, the cobalt-ammine ion is rapidly reduced to metallic cobalt at the electrode surface but the cobaltocysteinate ion may not be reduced to metallic cobalt. So the most delicate point in the interpretation of the whole catalytic electrode process involved in the polarographic "protein wave" consists in the elucidation of the role of cobalt. 3) Even if these waves depend on the catalytic reduction of hydrogen it is difficult to explain how, in the case of protein, two maxima are observed.

3) R. Brdicka, *Collection Czechoslov. Chem. Communs.*, 5, 148—164 (1933).

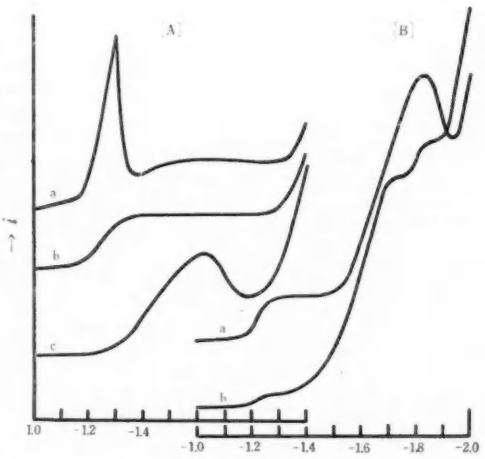

Fig. 1. Polarograms demonstrating the catalytic wave.
(A) a) $1 \cdot 10^{-2}$ M $CoCl_2$ + 1 M NH_4OH 1 ml. + 1 M NH_4Cl 1 ml. + H_2O 7 ml.
b) (a) + 1% gelatin 5 drops
c) (b) + H_2S
(B) a) (A, b) + $1 \cdot 10^{-2}$ M cystine 1 ml.
b) (a) + 1% methyl cellulose 10 drops

However, the coexistence of constituents (cobalt ion, cystine, carbohydrate, gelatin and ammonia) in the ammoniacal buffered solution is necessary to obtain the wave analogous to the protein wave. In view of the above experimental facts, it seems reasonable to assume that these five essential constituents in the ammoniacal buffered

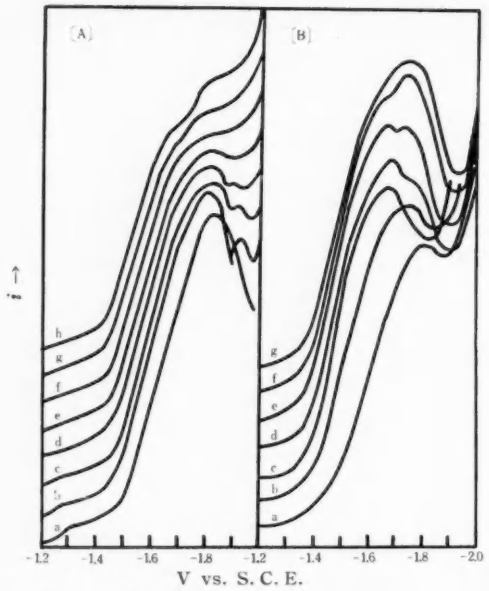

Fig. 2. Polarograms demonstrating the influence of methyl cellulose and gelatin on the cystine wave.

(A) 1% methyl cellulose 30 drops+10^{-2} M $CoCl_2$ 0.5 ml.+1 M NH_4OH 1 ml.+1 M NH_4Cl 1 ml.+H_2O: total volume 10 ml. $2\cdot10^{-2}$ M cystine:
a) 0.03 ml., b) 0.06 ml., c) 0.12 ml., d) 0.18 ml., e) 0.24 ml., f) 0.30 ml., g) 0.36 ml., h) 0.42 ml.

(B) a) $2\cdot10^{-2}$ M cystine 0.1 ml.+10^{-2} M $CoCl_2$ 0.5 ml.+1 M NH_4OH 1 ml.+1 M NH_4Cl 1 ml.+H_2O: total volume 10 ml.
b) (a)+1% methyl cellulose 1 drop
c) (a)+1% methyl cellulose 2 drops
d) (c)+1% gelatin 2 drops
e) (d)+1% gelatin 2 drops
f) (e)+1% gelatin 2 drops
g) (e)+1% gelatin 2 drops

system make a certain contribution to the electrode reaction either through their chemical interactions in the vicinity of the electrode surface and their adsorptive activities at the surface.

In conclusion, this mechanism may be considered in terms of the two following ideals: a) There may be some competition among the constituents which react with the cobaltous ions to yield complex ions or salts of extremely low solubility. Such competition in the vicinity of the electrode surface has a great effect on the currents of electroreduction and reoxidation of cobalt. b) The surface activities of these competing constituents have characteristic effects on the currents.

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Note on the Monomeric Friction Coefficient of Poly-n-butyl Methacrylate in Diethyl Phthalate

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From dynamic mechanical measurements encompassing the glass to rubber transition region Saunders et al.[1] have recently shown that the monomeric friction coefficient ζ_0 (in dyne sec./cm.) of poly-*n*-butyl methacrylate in diethyl phthalate at 0°C varied with the polymer concentration c (in g./ml. of solution), according to the relation:

$$\zeta_0 = 5.8\times10^{-10}\exp(24c) \qquad (1)$$

They state that there appears to be no theoretical expectation for the form of this relation. The purpose of the present communication is to show that their ζ_0 data can be interpreted reasonably in terms of a free volume theory described recently by Fujita and Kishimoto[2], if the original theory is modified so that the diluent concentration C (in grams of diluent per gram of dry polymer) is replaced by the volume fraction of diluent v[3]. Thus, the starting assumption of the modified theory is that the fractional free volume, f, in the polymer-diluent mixture at a fixed temperature T is a linear function of v, i.e.

$$f = f(T, 0) + \beta'(T)v \qquad (2)$$

where $f(T, 0)$ is the free volume fraction in the pure polymer at temperature T and

1) P. R. Saunders, D. M. Stern, S. F. Kurath, C. Sakookim and J. D. Ferry, *J. Colloid Sci.*, **14**, 222 (1959).
2) H. Fujita and A. Kishimoto, *J. Polymer Sci.*, **28**, 547 (1958).
3) The modification of the original theory, involving derivations of the new equations, and applications of the modified theory to viscosity data on concentrated polymer solutions will be described in detail in a forthcoming publication.

$\beta'(T)$ is a parameter (dependent on temperature) similar in nature to the parameter β defined previously[2]. The physical meaning of the new parameter β' will be given in a forthcoming article[3].

If one starts with Eq. 2 and uses a similar procedure to that described in Ref. 2, one can derive the relation:

$$-\frac{2.303[f(T,0)]^2 \log a_v}{1+2.303 f(T,0)\log a_v} = \beta'(T)v \qquad (3)$$

Here a_v is the concentration shift factor with the pure polymer as a standard and may be evaluated, in a manner described previously[2], from appropriate viscoelastic measurements obtained as a function of diluent concentration. Eq. 3 may be rewritten in the form:

$$-(1/\log a_v) = 2.303 f(T,0) + \{2.303[f(T,0)]^2/\beta'(T)\}(1/v) \qquad (4)$$

This indicates that plots of $-1/\log a_v$ vs. $1/v$ form a straight line and $f(T, 0)$ and $\beta'(T)$ can be determined from its slope and intercept at $1/v=0$.

Under the assumption that all the relaxation mechanisms—at least, those contributing to the mechanical behavior in the particular region concerned—have the same dependence on diluent concentration in the polymer, the shift factor a_v may be evaluated from the ratio of the monomeric friction coefficient of the mixture at diluent concentration v to that of the pure polymer ($v=0$) at the same temperature. The authors calculated a_v for the system poly-*n*-butyl methacrylate + diethyl phthalate at 27°C (this is the glass transition temperature of pure poly-*n*-butyl methacrylate[4]) from the ζ_0 data of Saunders et al.[1] and of Child and Ferry[4]. The latter study gives the ζ_0 values for the pure polymer at 27°C. The former data, which were originally given for the temperature 0°C have been converted to the desired temperature by using the WLF equation[5] with the numerical constants recorded in Table II of Ref. 1. Fig. 1 shows the plot of $-1/\log a_v$ vs. $1/v$ obtained from these data. It is seen that the plotted points follow a straight line reasonably well, in agreement with the prediction of Eq. 4. From the solid line drawn one finds that $f(T_g^0, 0)=0.023$ and $\beta'(T_g^0)=0.05_0$; here T_g^0 denotes the glass transition temperature of the pure polymer. It is of interest to see that the value of $f(T_g^0, 0)$ obtained, which was denoted by f_g^0 in Ref. 2, is quite close to the approximately) universal value 0.025.

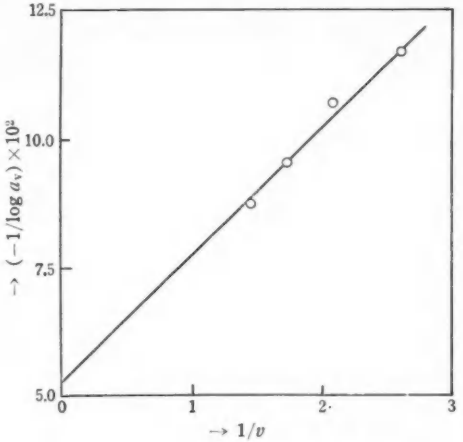

Fig. 1. Plot of $-1/\log a_v$ vs. $1/v$ for the system poly-*n*-butyl methacrylate + diethyl phthalate at 27°C; v is the volume fraction of diethyl phthalate in the mixture.

Eq. 4 may be used to evaluate $f(T, 0)$ and $\beta'(T)$ when the steady-flow viscosity, η, of the polymer-diluent mixture is known as a function of diluent volume fraction v. In this case the shift factor a_v may be taken as the ratio $\eta/[(1-v)\eta_0]$, where η_0 is the value of η for the pure polymer at the same temperature T. The authors applied Eq. 4 to Bueche's data[6] for the steady-flow viscosity on the system polymethyl methacrylate + diethyl phthalate at 100°C, the glass transition temperatue of this polymer[7]. A very satisfactory straight line was obtained between $-1/\log a_v$ and $1/v$ and yielded $f(T_g^0, 0)=0.017$ and $\beta'(T_g^0)=0.051$, where $T_g^0=100$°C. This low value of f_g^0 is consistent with a similar low value obtained previously[7] for this methacrylate polymer. Of interest is the result that the β' value derived here is very close to the one obtained above from the analysis of the friction coefficient data for the poly-*n*-butyl methacrylate + diethyl phthalate system. Although the definite conclusion must be reserved, it appears that to a first approximation the parameter $\beta'(T)$ is characteristic of the diluent

4) W. C. Child, Jr. and J. D. Ferry, *J. Colloid Sci.*, **12**, 327 (1957).
5) M. L. Williams, R. F. Landel and J. D. Ferry, *J. Am. Chem. Soc.*, **77**, 3701 (1955).
6) F. Bueche, *J. Applied Phys.*, **26**, 738 (1955).
7) H. Fujita and A. Kishimoto, *J. Colloid Sci.*, **13**, 418 (1958).

species, when camparison is made at T_g of respective polymers.

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Evolution of Atomic Oxygen from Platinum Surface Treated Previously with Discharged Oxygen Gas

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Fryburg[1] investigated an enhanced oxidation of platinum by treating a platinum strip with discharged oxygen gas at a temperature of 1000°C. He found that when the temperature of a platinum strip is higher than 800°C, a brown deposit of platinum dioxide appears on the wall of the enclosing glass tube in the immediate vicinity of the heated platinum strip.

After treating platinum surface with discharged oxygen gas, it is found that atomic oxygen evolves from it when heated in vacco.

The main part of the apparatus is shown in Fig. 1. D is a discharge tube. The reaction vessel V contains a platinum ribbon (0.024×0.28×363 mm.) capable of being heated by electric current. Atomic oxygen given off is detected by the change of color of molybdenum trioxide deposited on a glass plate P according to the following equation[2]:

$$3\,MoO_3 + O = Mo_3O_8 + O_2$$

Discharged oxygen gas is made to pass through the reaction vessel at a pressure of 0.1~1 mmHg for 20 min., without heating the platinum ribbon by electric current. Then the discharge being stopped, the

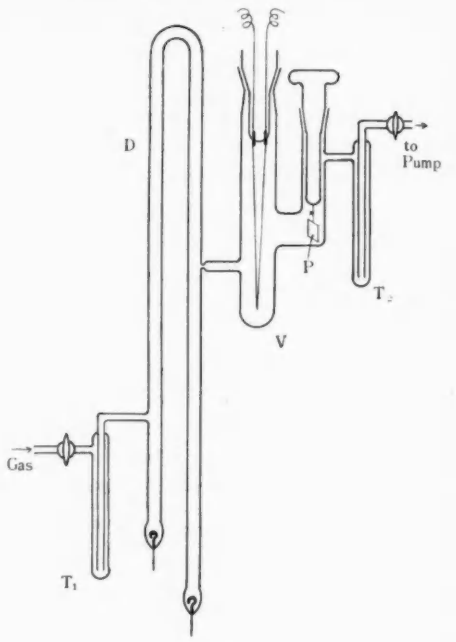

Fig. 1

reaction vessel is evacuated by a diffusion pump through a trap cooled by dry ice. In this condition, molybdenum trioxide remains to be pale yellow. While the evacuation is continued, the platinum ribbon is heated to 1400°C. Then, molybdenum trioxide in the side tube changes its color distinctly from pale yellow to deep blue within 20 min. This is an evidence that atomic oxygen is given off from the platinum surface. The authors will report in a later paper that adsorbed oxygen atoms desorb in molecular form when heated in vacuo. Therefore, taking account of Fryburg's experement[3], it is believed that the platinum surface covered with platinum dioxide, and that atomic oxygen is given off by the decomposition of platinum dioxide when the ribbon is heated to a high temperature in vacuo.

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1) G. C. Fryburg, *J. Chem. Phys.*, **24**, 175 (1956).
2) W. H. Rodebush and W. A. Nichols, *J. Am. Chem. Soc.*, **52**, 3864 (1930).
3) Loc. cit.